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ANALYSIS AND OPTIMIZATION OF A NEW METHOD FOR CREATING SANDWICH COMPOSITES USING POLYURETHANE FOAM

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ÉCOLE POLYTECHNIQUE DE MONTRÉAL

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Ce mémoire intitulé :

ANALYSIS AND OPTIMIZATION OF A NEW METHOD FOR CREATING SANDWICH COMPOSITES USING POLYURETHANE FOAM

présenté par : TRUDEAU Paul Arthur

en vue de l'obtention du diplôme de : Maîtrise ès sciences appliquées

a été dûment accepté par le jury d'examen constitué de :

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DEDICATION

To my parents who always encouraged me, my children and especially my wife Gisèle who is my inspiration.

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RÉSUMÉ

Les matériaux composites polymériques sont largement utilisés dans l'industrie moderne. Un composite sandwich est un matériau composite qui intègre un noyau de faible densité avec deux peaux opposées renforcée de fibres. Dans l'industrie aérospatiale les composites « sandwich » sont couramment utilisés pour une large gamme d'applications, dans le fuselage, les ailes ainsi que dans les panneaux décoratifs de l'intérieur. En général, pour les applications structurelles, les renforts d'aramide ou d'aluminium sous forme de nid d'abeille sont utilisés. Ces structures de haute technicité ont d'excellentes propriétés mécaniques. Cependant, les équipements et les procédés utilisés sont dispendieux et laborieux, ce qui entraîne des temps de cycle long, limitant ainsi le volume de production. Les composites «sandwich» sont aussi largement utilisés dans d'autres domaines come l'industrie automobile, l'industrie navale ou les industries des produits récréatifs. Pour ces applications à haut volume de productions, des procédés couteux sont utilisés. Cependant, ces procédés sont limités en termes de propriétés mécaniques ou en volume de production.

Il en résulte donc, un besoin grandissant de trouver une technologie capable de produire des composites « sandwich » en grand volume, avec de bonne propriété mécanique.

Ce projet de recherche vise l'étude d'un nouveau procédé de fabrication de composite « sandwich » en utilisant une mousse polyuréthane comme matériau de base, des fibres de verre comme renforcement et des peaux thermoplastique. Ce procédé de fabrication est une convergence de plusieurs procédés come le thermoformage, le préformage utilisant des adhésifs sensibles aux rayons ultraviolet, et l'injection de mousse polyuréthane.

Le procédé développé dans ce travail a été tentée dans le passé. Cependant, pour des raisons économiques, son développement a été arrêté. À cette époque, le procédé n'était pas optimisé. Les pièces fabriquées étaient de mauvaise qualité dimensionnelle avec de faible propriété mécanique.

L'objectif scientifique de ce projet, était le développement d'outils de caractérisation du procédé, afin d'étudier et mieux comprendre les mécanismes de moussage sous pression et d'imprégnation des tissues. L'approche scientifique utilisé a consisté à établir quatre plans d'expériences dans le but de: a) Caractériser le moussage du polyuréthane à l'aire libre ; b) Caractériser le moussage sous pression dans une cavité fermée ; c) étudier la formation de la mousse dans une cavité

tridimensionnelle ; d) fabriquer des composites « sandwich » ayant une forme géométrique complexe.

Dans ce travail, une cellule de production a été conçue et installée de manière à compléter le projet de recherche. Le coût total de l'installation a dépassé 300.000 dollars.

Ce travail a été présenté à la Conférence L'Association canadienne de l'industrie des plastiques (ACIP) de Montréal, (octobre 2008). Un document technique intitulé « Optimisation de l'imprégnation des fibres dans un nouveau concept de fabrication de composite sandwich en mousse polyuréthane » a été présenté au FPCM10 à Ascona en Suisse, (Juillet 2010). Deux documents supplémentaires seront soumis pour publication à l'automne 2010.

ABSTRACT

Polymer composite materials are widely used in modern industry. A sandwich composite is a composite material that integrates a low density core with two opposing reinforced skins. In the aerospace industry sandwich composites are commonly used for a wide range of applications, from fuselage and wing skins to interior decorative panels. However, most technologies for manufacturing sandwich structures are either rapid, resulting in reduced piece costs but with poor mechanical properties or the technologies are time-consuming resulting in high piece costs. There is need for cost effective, rapid processing that can produce sandwich composites with engineered properties.

This research project focuses on analysis and optimization of a new process for manufacturing sandwich composites using polyurethane foam as the core material, engineered fibreglass and engineered thermoplastic skins. This process is a convergence of several processes including thermoforming, preforming using ultraviolet binders and polyurethane foam injection.

The scientific goal was to develop characterizing tools for the process in order to fully understand the foaming and fibre impregnation mechanisms in a closed mould. In the scientific study, four plans of experiments were carried out: a) characterize the free rise foaming, b) characterize the foaming under pressure, c) understand the foaming behaviour in a three dimensional mould, and d) study the fabrication of a sandwich composite assembly.

In this work, the production cell was conceived and capital was procured in order to complete the research. The total cost of the installation exceeded $300,000. The project launched in the spring of 2008 and was ready for moulding trials by the fall of 2009.

This project was introduced (Oct. 2008) at the Canadian Plastics Industry Association Conference in Montreal. Also, (July 2010) a technical paper on the fibre wetting phenomena was presented at the FPCM10 Conference in Ascona Switzerland. Two additional papers will be submitted for publication in the fall of 2010.

CONDENSÉ EN FRANÇAIS

Étant donné leur faible masse et leurs bonnes propriétés mécaniques, les matériaux composites sont largement utilisés aujourd'hui pour remplacer l'acier et d'autres matériaux métalliques dans la fabrication de pièces structurelles. Au 20^{ième} siècle l'usage de ces matériaux a connue un essor important et étant donné les coûts sans cesse grandissants de l'énergie, cette accroissement sera encore plus décisif dans un proche avenir, tout particulièrement pour les secteurs de l'automobile, de l'aéronautique et de l'aérospatial. Dans le domaine automobile, le temps de cycle et la robustesse de la fabrication sont des paramètres clés pour les besoins de production à grand volume et les structures de type sandwich sont très en demande. Cependant leur mise en œuvre est limitée soit par la lenteur et le coût important du procédé, soit par de faibles propriétés mécaniques lorsque la fabrication des pièces est rapide. Différents procédés sont utilisés pour produire ce type de composite tels le *Resin Transfer Moulding* (RTM), le moulage par compression (SMC), le *Vacuum Assisted Resin Infusion* (VARI) ou encore l'injection traditionnelle (FRP). La Figure 1-4 illustre les capacités de production des pièces suivant ces différentes techniques de mise en œuvre.

Le procédé RTM est utilisé pour la fabrication de pièces structurelles complexes dans les secteurs tels que l'aéronautique, l'aérospatial ou encore les transports. Cependant étant donné les pressions d'injection importantes requises pour l'imprégnation des fibres, ce procédé est limité pour des pièces de taille moyenne (en dessous de 5 m^2) et des volumes de production annuels maximaux de 30 000 pièces. Le VARI est une alternative au RTM pour laquelle le moule supérieur est remplacé par un film de plastique ou une membrane flexible. L'injection de la résine est alors réalisée par la création d'un différentiel de pression dans la cavité et le vide ainsi créé est aspiré de manière continue par l'évent. Ce procédé est utilisé autant pour la fabrication de grandes que de petites pièces dans moule à une seule face. Cependant le temps de cycle est long et la variabilité entre les pièces peut être importante. Ceci limite la capacité de production annuelle à 10 000 pièces. Le moulage par compression SMC est une autre technique de fabrication très répandue pour des applications semi structurelles dans les domaines de l'automobile et des transports. Lors de ce procédé, les fibres et la résine sont rapidement compressées ensemble sous presse à une pression de moulage pouvant atteindre 6.9 MPa. Ce type de fabrication a un temps de cycle très court étant donné que les fibres sont déjà pré-imprégnées avec la résine et qu'il est donc limité seulement par le temps de fermeture du moule.

Ce procédé permet une production annuelle importante de plus de 50 000 pièces. Cependant certains inconvénients subsistent tels que l'importance de l'infrastructure et des coûts liés à l'outillage ainsi que les faibles propriétés mécaniques des pièces fabriquées. La technique d'injection plus traditionnelle FRP consiste à mélanger une résine thermoplastique à des fibres courtes pré-coupées. Cette technique est limitée aux petites pièces de surface inférieure à 2 m^2 étant donné la pression importante requise pour l'injection due à la viscosité élevée de la résine chargée. La production annuelle peut atteindre 100 000 pièces pour une ligne de montage.

L'industrie de fabrication des matériaux composites a donc un besoin au niveau procédé pour la fabrication de pièces de taille moyenne à grande, pour un temps de cycle de production moyen. La nouvelle technologie de fabrication de composites de type mousse étudiée dans le cadre de ce projet Poly-Foam (PFSC) cible tout particulièrement ce type de besoin. Un procédé semi-automatisé utilisant de la mousse de polyuréthane (PUR) et un procédé *Structural Reaction Injection Moulding* (SRIM) a par le passé démontré un potentiel de fabrication de grandes pièces composites structurelles pour des pressions d'injection faibles et un temps de cycle annuel de près de 45 000 unités pour une ligne de production. La Figure 1-5 illustre les propriétés mécaniques résultantes des pièces produites avec le procédé de fabrication de composites sandwichs Poly-Foam, propriétés qui sont très semblables aux composites fabriqués selon des méthodes plus traditionnelles.

L'objectif de ce projet de recherche est d'étudier le nouveau procédé de fabrication Poly-Foam et réaliser des composites de structure sandwich en utilisant de la mousse de polyuréthane. L'objectif scientifique principal du projet est de caractériser et de comprendre le procédé ainsi que de définir les paramètres clés permettant d'optimiser le cycle de moulage et les propriétés mécaniques de la pièce résultante. Cette étude permettra de définir les capacités et les limites de cette nouvelle technologie et ouvrira la porte à ce nouveau procédé tout en apportant la connaissance scientifique du comportement complexe de moussage de la résine polyuréthane et de l'imprégnation des fibres.

La première étape du projet consiste à formuler un adhésif ultra-violet qui permettra de lier le mat de fibre de verre à l'enveloppe thermoplastique PC-ABS. La seconde étape est de développer les outils permettant de caractériser entièrement le déploiement de la mousse de polyuréthane. Cette stratégie implique deux processus : A) l'examen des caractéristiques de la montée libre de la

mousse afin d'optimiser la formulation de la résine; notamment le profil de vitesse, les variations de densité et le comportement exothermique. B) Développer des techniques pour examiner les caractéristiques de gonflement de la mousse dans un environnement pressurisé de manière à identifier des paramètres critiques durant le processus tel le changement de la viscosité dynamique, l'évolution de la température et la gélification en temps réel. La troisième étape est l'optimisation du procédé de gonflement de la mousse de polyuréthane pour la pièce réelle, le couvercle du hayon du camion, avec et sans la présence du renforcement de mat de fibre de verre. Le but est d'optimiser les propriétés mécaniques de la mousse et de la structure sandwich résultante.

Un composite sandwich est réalisé en combinant une enveloppe renforcée de fibres à un noyau de faible densité. Le but du noyau est d'augmenter l'épaisseur de la pièce tout en réduisant la masse totale de la structure. Le matériau sandwich résultant aura donc une grande rigidité spécifique et une robustesse élevée; en sous-entendant que la robustesse de la poutre est proportionnelle au carré de son épaisseur. Ceci permet une grande polyvalence au niveau de la conception des pièces. A titre d'exemple, le composite sandwich peut être utilisé pour des raisons purement structurelles où la réduction de la masse est la priorité ou encore pour lui conférer des propriétés spécifiques telles que l'amortissement aux vibrations et au bruit, une amélioration de l'isolation ou une meilleure résistance à l'impact. Les matériaux constituants le sandwich sont les fibres, la résine, le noyau de mousse et éventuellement l'enveloppe thermoplastique. De même que pour les composites structurels standards, les fibres sont les composantes qui supportent la plupart des charges tandis que la matrice facilite le transfert des contraintes entre les fibres et le noyau. Bien que le noyau doive idéalement être le plus léger possible, il faut cependant qu'il puisse transmettre les forces au travers de la structure sandwich. Il doit donc être résistant lors de l'application de forces en tension ou compression. L'enveloppe est utilisée principalement pour des raisons cosmétiques ainsi que pour certains besoins spécifiques liés à l'exposition de la pièce à l'environnement comme la résistance chimique, la résistance à la température ou encore à la teneur en flammabilité.

Les mousses de polyuréthane (PUR) et de polyisocyanate (PIR) sont les plus couramment utilisées dans la mise en forme de structures sandwich. Le PUR et le PIR sont synthétisés par une réaction entre un monomère ayant deux groupes fonctionnels alcools (OH) avec un monomère

ayant deux groupes fonctionnels cyanate (NCO), en la présence d'un catalyseur. Les émanations de styrène de même que de composés organiques volatils (COV) sont exclues de la réaction chimique, ce qui est un avantage écologique important comparativement à l'utilisation de mousses à base de chlorure de polyvinyle (PVC) ou de styrène acrylonitrile (SAN), lesquelles sont connues pour leurs émanations de styrène et de chlore et donc sujettes aux normes strictes EPA [12]. Un autre avantage dans l'utilisation de PUR ou de PIR est la facilité à laquelle la structure chimique peut être modifiée de manière à rencontrer les propriétés thermiques et mécaniques souhaitées. Ces matériaux présentent notamment une large gamme de dureté, de densité et de raideur. Il existe aussi plusieurs procédés de mise en forme possibles pour le PUR et le PIR tels que le moulage par injection réactive (RIM), la lamination continue, le gonflement de mousse par dalle ou boîte. L'un des avantages majeur dans l'utilisation de ces mousses est la possibilité de mouler des formes très complexes en réduisant la quantité de rebus, d'usinage ainsi que les opérations de formage.

Les mousses PUR réagissent et polymérisent rapidement comparativement à d'autres types de mousses thermodurcissables telles les syntactiques (époxides). Bien que le temps de polymérisation dépende de l'épaisseur et de la densité, dans la plupart des applications, les mousses PUR peuvent être démoulées en quelques minutes (8-20 minutes) par rapport aux mousses de types syntactiques pour lesquelles cela prend des heures.

Il y a cependant des limites à la création de structure sandwich à base de mousse de polyuréthane notamment au niveau du capital d'investissement important nécessaire à la mise en place du moule de fabrication. Une ligne typique de production est constituée d'une unité robotisée pour l'insertion des matériaux, d'un convoyeur, d'un four de cuisson, d'un système assisté pour l'ouverture et la fermeture du moule, d'une aire de nettoyage et d'application d'agent démoulant ainsi qu'une aire pour l'insertion des différents accessoires allant sur la pièce composite fabriquée. Le retour sur le capital d'investissement requiert donc une production à grande échelle.

Les mousses PUR et PIR ont de bonnes propriétés en compression et des propriétés physiques modérées lorsqu'on augmente leur densité. Cependant, les mousses de faible densité ont tendance à être friables et ont donc une faible résistance à l'abrasion et une faible tenue en fatigue dans le temps. Dans l'industrie marine, ce type de mousse à haute densité et faible friabilité est très utilisé pour la fabrication des impostes séparant les différentes aires de la coque, étant donné son

importante force en compression, tandis que les mousses de plus faible densité sont utilisées pour fabriquer les longerons [12].

La réaction rapide de polymérisation des mousses PUR et PIR peut cependant amener des difficultés au niveau de la fabrication. Dans le cas du SRIM où la résine PUR est injectée au travers de la préforme de fibres, deux problèmes peuvent subvenir; premièrement la viscosité initiale importante du PUR qui peut rendre difficile l'imprégnation de la préforme. Deuxièmement, l'augmentation très rapide de la viscosité durant la polymérisation limite la saturation des fibres. Pour ces raisons, le procédé SRIM n'a pas une croissance aussi importante que souhaitée dans l'industrie du composite.

Le préformage des fibres pour l'injection liquide est une étape critique dans la fabrication de la pièce composite. L'orientation des fibres est cruciale dans la fabrication de composites à haute performance et seuls certains procédés sont capables d'en tenir compte. Des couches de tissu sec sont découpées, alignées et maintenues ensemble par des adhésifs, des résines ou des poudres thermoplastiques. La consolidation peut se faire à l'aide un moule à une seule face par l'entremise d'une membrane ou alors avec moule standard à deux faces. Les options de préformage sont plus diverses pour la fabrication de composites de basse performance. Citons le thermoformage à volet continu de mat avec un moule à deux faces, la pulvérisation de fibres coupées par l'entremise d'un liant de type poudre sur des écrans sous pression suivie d'une consolidation dans un moule à deux faces et d'une cuisson, et bien d'autres.

Le préformage par cuisson sous ultraviolets (UV) a été choisi dans le cadre de ce projet pour la fabrication du composite sandwich selon le procédé Poly-Foam. Des tissus d'ingénierie sont utilisés afin d'obtenir des pièces à hautes performances mécaniques. Il est aussi important que le procédé puisse être répété, soit rapide et puisse également intégrer des tissus d'ingénierie de type mat. De plus, il est nécessaire d'avoir un procédé semi-automatisé afin de pouvoir rencontrer l'objectif de production annuelle de 45 000 pièces pour une seule ligne de production ou encore un cycle de production maximal de 8 minutes par pièce. Étant donné que les fibres du procédé PFSC sont placées des deux côtés de l'enveloppe thermoplastique, le procédé de préformage seul peut dépasser les 4 minutes par enveloppe. Pour remédier à cela, il faut donc que la cellule de préformage soit conçue de manière à ce que l'adhésif UV soit pulvérisé à l'aide d'un robot sur la peau thermoplastique constituant l'enveloppe. L'opérateur peut par la suite placer directement le

tissu mat sur la surface pulvérisée de l'enveloppe. Finalement une membrane est utilisée afin de comprimer les fibres contre l'enveloppe, le tout suivi d'un ensachage sous vide. La pièce est acheminée dans la chambre UV par un automate.

Au niveau du développement et de la caractérisation du procédé UV réalisés dans ce projet, les paramètres de réglage optimum du convoyeur sont une distance de 30 cm entre les lumières UV et la pièce et une vitesse de convoyeur de 45 mm/min. En utilisant ces paramètres, la cuisson d'un échantillon ave une simple couche de fibre de verre demande un dosage de l'adhésif UV de plus de 1000 mJ/cm^2 afin d'en assurer la cuisson en profondeur.

Trois adhésifs UV différents ont été caractérisés et un nouveau matériau a été développé et commercialisé conjointement avec la société Inortech Chimie. Le nom de commerce de ce nouveau liant est CB-601. Des tests de pelage ont été réalisés de même que essais en caractérisation dynamique mécanique (DMA) et en calorimétrie à balayage différentiel (DSC) afin de déterminer la température de transition vitreuse *Tg* des adhésifs. L'énergie de débondage du liant CB-601 est supérieure à tous les autres adhésifs caractérisés de même que le module élastique pour les températures étudiées et la température *Tg* est de l'ordre de 50°C.

Les mousses de polyuréthanes permettent de réaliser une grande variété d'applications structurelles étant données la possibilité d'avoir des propriétés sur mesure allant de mousses très élastiques à rigides en passant la viscoélasticité. De même il est possible de fabriquer des pièces 3D complexes par moulage avec des propriétés très spécifiques. Dans le cadre de ce projet, la chimie du polyuréthane utilisé a été développée de manière a obtenir une mousse rigide. Des isocyanates polymériques (pMDI) ont été mélangés selon des proportions non-stochiométriques à des polyols polyether. La mousse de polyuréthane ainsi formulée est de la famille des isocyanurate et le mélange est fait de manière à ce qu'il y ait un excès d'isocyanate lors de la polymérisation avec le catalyseur. L'isocyanate en excès réagit par la suite avec lui-même afin de rigidifier encore plus la mousse de polyuréthane et ainsi améliorer le module élastique de même que *Tg*.

La mousse de polyisocyanate est déployée en utilisant un agent gonflant à base d'hydro-fluorocarbone (HFC) combiné à de l'eau. Grâce à cet agent, la viscosité de la mousse de

polyuréthane est réduite, ce qui facilite le mouillage des fibres durant le procédé d'imprégnation. De plus son utilisation n'affecte pas la couche d'ozone et n'émet pas de gaz à effet de serre.

Afin d'optimiser la formulation de la résine PUR, quatre plans d'expérience ont été réalisés, ce afin de comprendre le mécanisme de formation de la mousse de même que les interactions entre ses différents composants. La proportion de résine a été optimisée de manière à obtenir les propriétés mécaniques souhaitées.

Dans le premier plan expérimental, la mousse a été caractérisée sous pression atmosphérique. Les analyses à ce stade ont permis de comprendre le gonflement de la mousse et de caractériser sa densité pour des formulations établies selon des proportions stœchiométriques. Les appareils utilisés pour la caractérisation sont présentés à la section 4.3 et le montage expérimental est présenté à la Figure 4-4. Le mélange de résine est injecté dans un contenant de 20 litres et le profil de montée de la mousse est mesuré à l'aide d'un capteur de distance Senix® ToughSonic®/PC. La température a été mesurée à l'aide de thermocouples de type J et les émanations gazeuses à l'aide d'une balance de précision. La Figure 5-1(b) illustre le logiciel d'acquisition des donnés Labview qui permet la mesure en temps réel de la température, la montée de la mousse ainsi que la perte de gaz durant le gonflement de la résine. Une photo d'une pièce moulée est illustrée à la Figure 5-1(c).

L'objectif du second plan expérimental était de comprendre les effets du changement de pression, la réaction exothermique et la viscosité dynamique de la mousse lorsque cette dernière était soumise à une polymérisation sous pression dans un moule fermé. Cette étude a été réalisée à l'aide du moule présenté à la section 4-4. La pression dans le moule est tout d'abord réduite de manière à atteindre un vide presque total avant l'injection de la résine. Une pièce de mousse avec de la fibre de verre réalisée sous ces conditions est illustrée à la Figure 4-15. Le plan d'expérience (*Design of Experiment* - DOE) comprend 2 variables ayant chacune 3 niveaux, soit l'indice d'isocyanate (120-130-140) et la densité de la mousse (192-224-256 kg/m^3). Afin de pouvoir suivre les changements de viscosité durant la formation de la mousse, le changement de la viscosité ionique a été enregistré, de même la pression en temps réel et la température. Des mesures physiques ont également été réalisées telle la densité, les épaisseurs de l'enveloppe et du laminé. Les paramètres du procédé sont les mêmes que pour le premier plan expérimental et sont décrits au Tableau 5-1. Le résultat de l'imprégnation des fibres est illustré à la Figure 5-11. Tous

les résultats sont résumés au Tableau 5-5. Des résultats obtenus il ressort que l'effet de l'indice est beaucoup moins significatif que celui de la densité. Le meilleur mouillage des fibres a été réalisé pour un indice de 130 et une densité de 224 kg/m^3. La saturation des fibres de verre est améliorée lorsque la densité de la mousse augmente tandis que la variation de l'indice d'isocyanate n'a pas d'influence marquée sur le mouillage résultant des fibres. Ceci suggère que l'agent de gonflement est probablement en quantité insuffisante pour créer le phénomène de mouillage des fibres et est traduit par une montée de pression supérieure à 300 kPa au Tableau 5-5. Dans la colonne de gauche du Tableau 5-5 où la densité est constante à 192 kg/m^3 et l'indice variable e 120 et 140, la saturation des fibres est faible ainsi que l'épaisseur résultante de l'enveloppe autour de 1.1-1.3 mm. A cette valeur de la densité, la pression mesurée (244 kPa pour un indice de 120 et 225 kPa pour un indice de 140) pour qu'il y ait gélification est insuffisante pour mouiller les fibres. Cette chute de pression est une conséquence de la diminution du pourcentage d'agent gonflant et des catalyseurs tel que montré par la décroissance de la valeur de l'indice. Pour développer la meilleure structure sandwich, les propriétés du laminé et de la mousse doivent être combinées lors de l'optimisation. L'augmentation de l'indice améliore les propriétés mécaniques de la mousse mais rend le mouillage des fibres plus difficile et augmente la densité ce qui rajoute de la masse et donc un coût à la pièce.

Le troisième plan expérimental est réalisé sur une pièce 3D et l'accent est mis sur la mesure des propriétés mécaniques de la pièce. L'impact des propriétés mécaniques et étudié en fonction des deux variables du plan d'expérience précédent soit l'indice d'isocyanate et la densité de la mousse. A cela vient s'ajouter un troisième paramètre, la température du moule. Quinze injections ont été réalisées suivant deux indices d'isocyanate (120, 140), trois niveaux de densité (192, 224 et 256 kg/m^3) et deux températures du moule (35 et 40°C). La cavité du moule est conçue de manière à ce que les trois composantes de la pièce puissent être réalisées simultanément à chacune des injections. Pour cette raison, trois tête d'injection de résine PUR ont été installées sur le moule supérieur et ont été attachées au plateau supérieur de la presse hydraulique. Chacune de ces têtes est liée aux ports d'injection des cavités du moule.

Les analyse du quatrième plan expérimental on été réalisées sur les composites de structure sandwich renforcée de fibre de verre. La quantité de variables des expériences précédentes a été réduite et ce nouveau plan d'expérience a été conçu de manière à évaluer l'impact de la

formulation de la résine sur le mouillage des fibres les propriétés mécaniques de la mousse. Seules deux variables ont été étudiées : l'indice d'isocyanate et la densité de la mousse.

En conclusion, le procédé Poly-Foam présente une méthode de fabrication innovatrice pour la réalisation de composites de structure sandwich à haute performance. Cette fabrication est plus écologique et permet de produire annuellement près de 45 000 pièces pour une ligne de production. Ce procédé est automatisé notamment par l'utilisation de robots pour le transport des enveloppes thermoplastiques et des fibres, ce qui simplifie le moulage et réduit le temps de nettoyage. Les pièces fabriquées ont la texture et la couleur désirée dépendamment de l'enveloppe choisie sans qu'il soit nécessaire par la suite de recourir à des étapes de sablage et de peinture. De la même manière, les propriétés de résistance aux conditions environnementales de l'enveloppe peuvent être ajustées sur mesure.

L'innovation importante apportée par ce procédé est l'injection de la mousse de polyuréthane directement à l'intérieur de la préforme constituée de l'enveloppe thermoplastique et des fibres, ce qui permet le moulage d'un composite sandwich en une seule étape. La nature même de la mousse de polyuréthane (formation d'une peau durant la polymérisation) rend possible la création d'un noyau 3D de mousse qui permet lui permet de mouiller les fibres tout en se rigidifiant.

Le développement d'un procédé de préformage avec des adhésifs UV permettant de coller le mat de fibres à l'enveloppe thermoplastique offre un large éventail de formulations dépendamment du substrat thermoplastique choisi. Grâce à ce procédé, il est possible de polymériser les adhésifs à basse température, ce qui réduit ainsi les contraintes et les distorsions éventuelles de l'enveloppe. Ce procédé se prête également à l'automatisation.

L'objectif principal de ce projet de recherche qui était de caractériser entièrement le procédé de manière à bien comprendre le processus de mouillage des fibres et son impact sur les propriétés mécaniques finales de la pièce a été atteint. Différents équipements on été conçus et construits afin de pouvoir mesurer le comportement de la mousse sous pression atmosphérique et sous haute pression. Il a été possible grâce à cet appareillage de réaliser des essais en variant la formulation de la résine et les paramètres d'injection de manière à optimiser les conditions de fabrication. Les résultats obtenus pour les différents plans d'expérience réalisés illustrent que la pression qui se

développe dans la mousse elle-même définit le niveau de saturation. La densité et l'indice d'isocyanate optimums sont de valeurs médianes, soit 225 kg/m^3 pour un indice de 130. Ce résultat est encourageant étant donné qu'il est souhaitable pour des raisons économiques de réduire la densité permettant ainsi d'obtenir un composite de masse réduite. Contrairement aux structures sandwich de faible densité ou les propriétés du noyau ont un effet minime sur les propriétés résultantes de la pièce, dans le cas présent, ces propriétés ont une influence directe sur la rigidité finale du composite et sur son comportement en tension. Ceci est dû au fait que le toute la structure du laminé est relié au noyau. Une formulation de mousse a pu être optimisée dans le cadre de ce travail étant donné les techniques de caractérisation développées. Ceci permet d'envisager dans l'avenir l'utilisation de ce type de structure sandwich pour des applications à haute performance telles que dans le secteur aérospatial.

Cette recherche a ouvert les portes à différentes applications structurelles et semi-structurelles telle les planchers de chargement, les balcons, les systèmes de toiture, etc. En étant visionnaire, plusieurs secteurs pourraient profiter de cette technologie et différents produits pourraient être optimisés notamment en étant plus écologique par l'utilisation de bio-résines et de fibres naturelles. Afin de pouvoir utiliser ce procédé pour le domaine aérospatial, l'étape suivante est de procéder à des tests de flammabilité et améliorer le produit fini en conséquence. De plus, l'enveloppe thermoplastique nécessitera une optimisation ou un changement pour une enveloppe de la famille des polyimides. De nouveaux développements d'adhésifs devront être réalisés. Le procédé de structure sandwich à base de mousse PUR tel qu'il a été optimisé devrait permettre une réduction de masse et des améliorations manifestes des propriétés mécaniques.

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NOTATIONS

α	Degree of cure
$\dot{\alpha}$	Reaction rate (s^{-1})
ϕ	Porosity
v_f	Fibre volume fraction
P	Density (kg/m^3)
ρ_s	Areal weight (Kg/m^2)
σ_{renf}	Stress applied to reinforcement (Pa)
μ	Kinematic viscosity (Pa.s)
ν	Dynamic viscosity ($m^2.s^{-1}$)
$\mathbf{v}_D$	Darcy velocity ($m.s^{-1}$)
V	Observed Velocity ($m.s^{-1}$)
V	Velocity normal in general ($m.s^{-1}$)
T	Temperature (K)
T_{gel}	Gel Temperature (K)
Re_d	Reynolds Number
Q	Heat Flux (W/m^2)
K_1 et K_2	Principal Permeability values (m^2)
P	Pressure (Bars)
k	Conductivity ($W.m^{-1}.K^{-1}$)
h	Heat transfer coefficient ($W.m^{-2}.K^{-1}$)
ΔH_r	Total heat of reaction ($J.kg^{-1}$)
c_p	Specific heat ($J.kg^{-1}.K^{-1}$)
K	Permeability of a reinforcement (m^2)
Q	Volumetric flow rate (l/s)

Index

x , y , z	General reference
r	Resin
f	Fibres
m	Mould

Acronyms

LCM :	Liquid Composite Moulding
SMC/BMC:	Sheet moulding compound/bulk moulding compound
RTM/VARTM :	Resin Transfer Moulding/ Vacuum Assisted
VARI :	Vacuum Assisted Resin Infusion
SCRIMP:	Seeman Composites Resin Infusion Molding Process
FRP:	Fibre-reinforced Polymer
SRIM:	Structural Reaction Injection Moulding
RRIM:	Reinforced Reaction Injection Moulding
DMA:	Dynamic Mechanical Analyzer
DSC:	Differential Scanning Calorimeter
PFSC:	POLY-FOAM Sandwich Composite
VOC:	Volatile Organic Compound
LPA:	Low Profile Additive

CHAPTER 1 INTRODUCTION

The use of polymer composite materials in the industry has experienced significant growth during the 20th century. Thanks to their tailored mechanical properties and their low specific weights, composite materials are seen as a key alternative to common materials such as steel and other metals. Due to the rising cost of energy, the use of composites is expected to grow even faster, particularly in the automotive and aerospace industries. Energy efficiency is recognized as the greatest challenge facing these transport industries.

In the automotive industry, cycle time and robustness of the manufacturing processes are key indicators of the needs for high volume production. Sandwich structures are in demand in these industries; however, processing techniques for such composite parts are either slow and expensive or fast with low mechanical properties. For example, at Decoma International [1] semi-structural sandwich structures are fabricated using a pour and compression technique. In this simple process, polyurethane foam is sprayed on fibreglass preforms placed in open moulds (see Figure 1-1). In a second step, polyurethane foam is sprayed on the opposite mould half, as depicted in Figure 1-2. The mould is then closed followed by curing, (see Figure 1-3). Appropriate wetting of the fibreglass is one of the limitations of these technologies. Also, high void contents are usually obtained due to the air contained in the mould cavity after closure.

Figure 1-1 : Foam composite processing at Magna. Step 1, pour foam on lower mould [1].

Figure 1-2 : Foam composite processing at Magna. Step 2, pour foam on upper mould half [1].

Figure 1-3 : Foam composite processing at Magna. Step 3, close mould and cure part [1].

Within the many different techniques to manufacture structural composite parts there is Resin Transfer Moulding (RTM), Compression Moulding (SMC & BMC), Vacuum Assisted Resin Infusion (VARI), and Long-Fibre Injection Moulded Thermoplastics (LFTs). Figure 1-4 illustrates the production capabilities of these techniques. RTM consists of injecting a liquid resin through a fibrous reinforcement contained in a closed mould. This technique is used to make complex structural parts in industries such as aeronautic, aerospace, and transportation; however, due to the injection pressure required to impregnate the fibres, it is limited to parts of medium size (below 5 m^2) with production volumes not exceeding 30,000 parts per year. The VARI process is a variation of RTM in which the upper mould is replaced by a vacuum bag or plastic film. In this case resin is infused into the reinforcement due to a differential pressure created

when the air inside the cavity is removed by applying vacuum at a venting point on the part. This process can be used to make both large and small parts on single sided moulds. The cycle times are long and the variability from part to part can be high. This leads to maximum production capability up to 10,000 units per year. Compression moulding (SMC) is another technique widely used to manufacture composites in a thin shell form, mainly applied in semi structural applications for the automotive and transportation markets. In this technique resin and fibres are rapidly compressed together in high tonnage presses, reaching moulding pressures up to 6.9 MPa (1000 psi). L. Berger from General Motors recently published a paper using advanced SMC processing techniques to manufacture "A Structural Automotive Underbody", incorporating cores and advanced preforms [2]. This research is attempting to increase the mechanical properties realized using advanced SMC techniques.

The SMC process has very fast cycle times because the fibres are pre-impregnated with resin, therefore, cycle times are related to the closing speed of the equipment. This technique is capable of high production volumes of more than 50,000 parts per year. However, there are several drawbacks such as high infrastructure and tooling costs and low mechanical properties of the parts.

Finally, there is an emerging technique where short and long chopped fibres are mixed with thermoplastic resin, followed by direct injection into closed moulds, called Long-Fibre Injection Moulded Thermoplastics (LFTs). This technique is seeing increased use in the industry because of cycle time advantages; however, low mechanical properties and reduced part size capability remain the key issues [3].

This technique is limited to small parts below 2.5 m^2 due to the high injection pressures resulting from the elevated resin viscosities. Production volumes can reach 100,000 units per year from a single tool set. Similar to SMC moulding this process requires high cost infrastructure and the resulting mechanical properties are low.

From the two bubble charts shown in Figure 1-4, there is a need for a process that can produce medium to large composite structures at medium production rates. The new foam composite technology under investigation in this project, PFSC falls into this high need area. This semi automated process which utilizes polyurethane foaming and structural reaction injection moulding methods (SRIM) has shown potential to fabricate large composite structures at low

moulding pressures and with cycle times approaching 45,000 units per year out of a single tool set. As shown in Figure 1-5 the mechanical properties of parts made with the polyurethane foam sandwich composite process (PFSC) are close to those of traditional processes. Figures 1-4 and 1-5 illustrate the potential advantages of this new process over existing processing technologies.

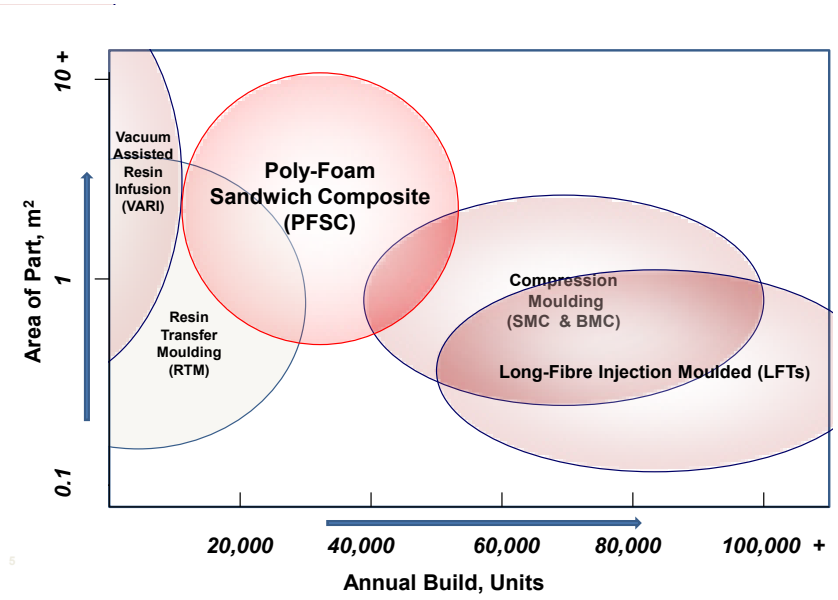


Figure 1-4: Part size and production volumes of different composite moulding techniques.

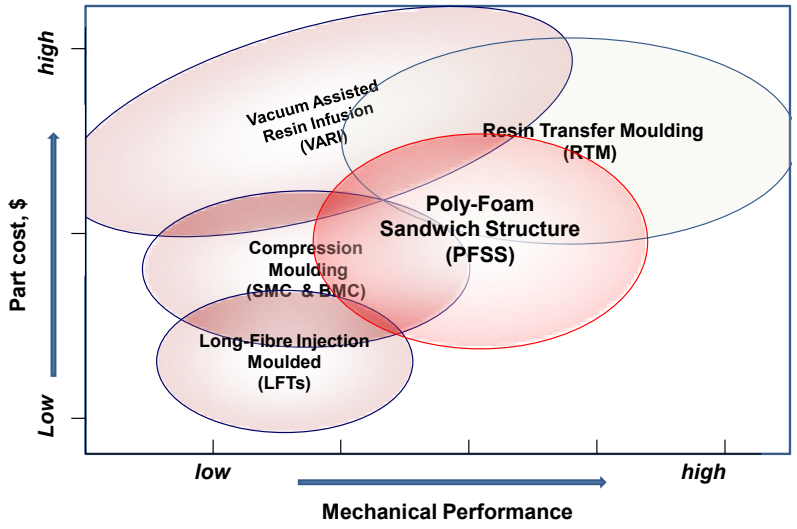


Figure 1-5: Cost and mechanical properties of composites manufactured with different techniques.

The polyurethane sandwich composite process proposed in this work was initially conceived in Connecticut by a small start-up company named Advance USA in 1998. Patents were filed in 2001 and awarded in 2006 [4]. The initial idea was conceived years earlier when manually building composite marine structures, while being exposed to chemical vapours, solvents and respirable dusts. At that time the idea was put forth, design a semi automated process which eliminates the need to paint and sand the final products, thereby eliminating or reducing the exposure to the chemicals and fibres. The process developed by Advance USA is shown in Figure 1-7 [6].

The solution which emerged involved a convergence of three processes. Thermoforming to create the outer skins of the product (see steps 1 to 3 on Figure 1-7), preforming to pre-attach the fibres to the skins (see steps 4 and 5) followed by injection of the polyurethane foam in a RIM mould (steps 6 and 7), to finally consolidate and create the multi layer 3D sandwich structure (step 8). The first part produced was 3.7 m long roof system for the Fleetwood Folding Trailer Division of Coleman (see Figure 1-6).

Figure 1-6 : Production cell for the 3.7 m long Coleman Camper roof system [5].

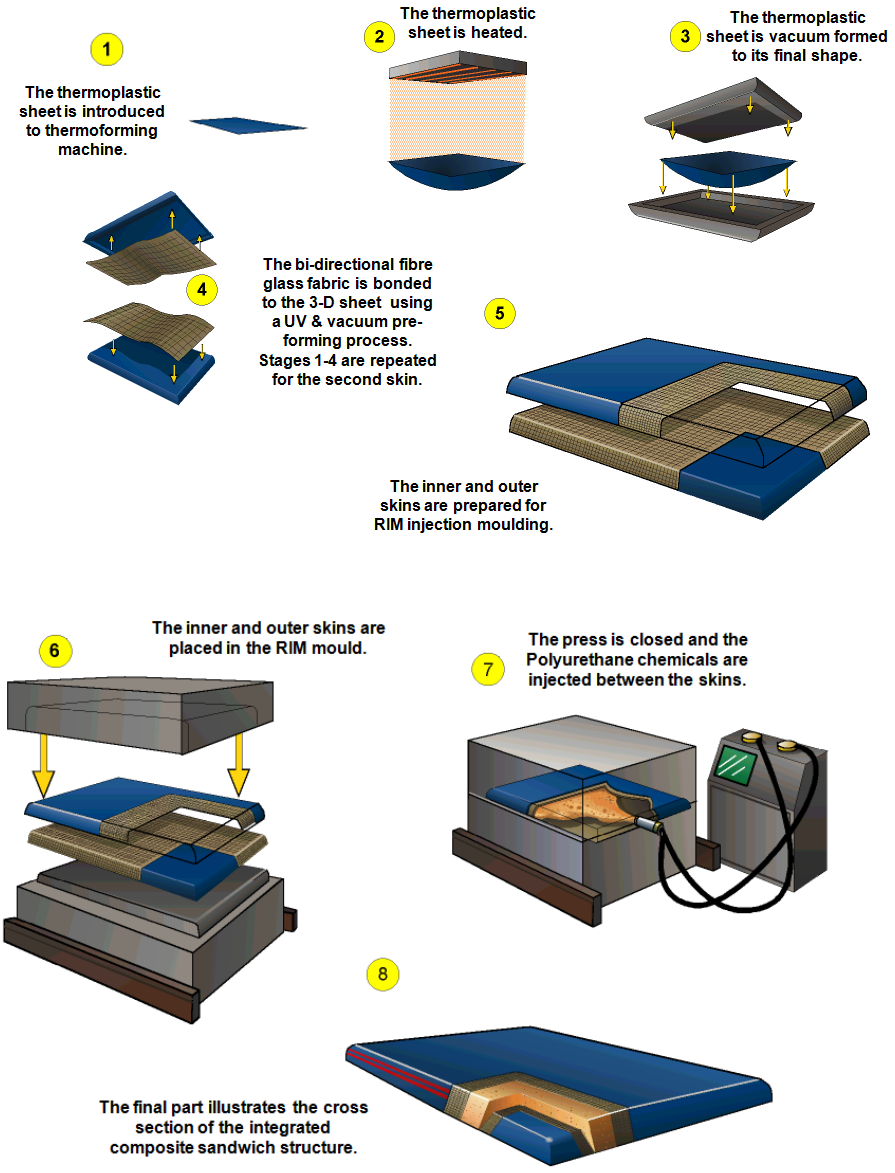


Figure 1-7 : Schematic of the Advance USA sandwich process, 1998 [6].

The initial products were made using ABS thermoplastic skins. Unidirectional fibreglass layers were bonded to the thermoplastic skins using a thermally cured urethane adhesive. The foam used to create the core was rigid polyurethane foam resin formulated by the Bayer Material Science group from Pittsburgh. Initially there were two commercial products: 3 m and 3.7 m roof systems built for Fleetwood Folding Trailers. In 2001 the second commercial product was launched, an interior sleeper bunk bed for Freightliner (see Figure 1-8).

(a) (b)

Figure 1-8 : Sandwich composite sleeper bunk in (a) down position and (b) stowed positions [6].

In 2001, the development of this novel technology was progressing with goals to launch another higher performance product, a truck box cover. At this time, there were problems with temperature capability of the structure, creep failures in the field, and high levels of customer returns due to blistering and cracks. Due to economic hardship in 2002 Advance USA went into receivership and was eventually closed in 2003. After the bankruptcy in 2004, Decoma International purchased select assets from the Advance USA receivers in an attempt to transfer the process in house. The target demonstration product was a multipurpose three piece truck box cover. Preliminary work was done to get the new product ready to show to customers. Some improvements were made to the structure which included improving the weatherability and temperature resistance of the thermoplastic skins. By 2005 the sales team was unable to secure a production order for this new technology; as a result so Decoma International decided to close the project and sell the assets. Through the Chair on Composites of High Performance (CCHP) and with funds from the Canadian Foundation for Innovation (CFI), École Polytechnique purchased a few of the key assets in order to bring this new technology in house.

1.1 OBJECTIVES OF THE RESEARCH PROJECT

Currently there are only a few methods capable of producing large sized advanced sandwich composites for medium to high production volumes rates as illustrated in Figure 1-4. Unfortunately, these processes result in products with generally low mechanical properties due to limitations in fibre volume fraction. For processes where material properties are higher, the manufacturing rates often decrease; such as with, VARI, RTM and SCRIMP. As well, with these processes there are some additional threats due the environmental regulations and the general

desire to reduce consumption of toxic materials, such as: chlorine, styrene, benzene and other VOC's. Therefore there is a growing need for new processing methods that will offer greener solutions, good mechanical properties and faster gel times.

The objective of this investigation is to study this new PFSC process used to fabricate sandwich composites using a PUR foaming technology. A thorough search in the literature will be conducted, specifically in the area of polyurethane composite sandwich structures and methods for producing sandwich composites and preforms.

The main objective of this research is to characterize the Poly-Foam Sandwich Composite process (PFSC) to scientifically understand its behaviour and define key parameters to optimize the moulding cycle, mechanical properties and production volume capabilities.

A series of designed experiments are planned in order to sequentially gain insight and knowledge about the process in order to effectively optimize the parameters and fully understand the mechanism of fibre saturation, the key to this novel technology.

The first research objective is to develop a new UV adhesive that will bond engineered fibreglass to PC/ABS, serving as a preforming binder. In this planned study a series of products will be screened in order to develop a baseline understanding of the material properties, curing requirements, and the thermo-mechanical behaviour. The primary objective of this work will be to minimize any negative interaction the binder may have in the composite when it is stressed or exposed to thermal loads.

The self skinning polyurethane chemistry is one of the enablers in this technology. Formulating polyurethane foams is well known in the art; however, this novel process involves controlling precisely when the foam cells adjacent to the surface of the mould collapse in order to form the skin and wet out the fibrous reinforcement.

The second objective is to develop tools to fully characterize the polyurethane foam system. The strategy involves two stages: 1) Examine the free rise characteristics of the foaming system in order to optimize the resin formulation; specifically the free rise foam velocity profile, free rise density variation, and exothermic behaviour. After completing this step the robustness of the formulation will be understood; also how changes in the stoichiometric proportions affect the foam morphology, stability, density and variability. This will also aid in establishing the

equipment processing parameters: flow rates, temperatures and pressures for the remaining experiments.

2) Due to the rapid curing behaviour of PUR foams traditional techniques for characterizing become difficult to use such as Differential Scanning Calorimetry (DSC) or Rheological testing. It is therefore necessary to develop techniques to examine the foaming characteristics under a pressurized environment. This will make it possible to identify the critical changes in the foam development such as changes in viscosity and the gel point, compared to the real-time pressure and temperature measurements of the foam. In this research stage there is a plan to design and construct a fully instrumented mould (impedance, pressure temperature), with a site window. This tool will bring insight into the curing and viscosity behaviour of the foam; as well, it will make it possible to view the saturation phenomena in real time.

When moving from a laboratory scale study to a full size part unforeseen effects are often observed. In this work, many of the parameters of this foaming process were modified including, chemical substitutions in the resin (new surfactant, and new catalyst), use of a new binder and re-establishing the machine parameters for injection, (pressures, temperatures and flow rates). To accomplish this task a series of simple moulding experiments must be completed in advance of the planned experiments. This will make it possible to minimize the number of variables in the experiments, therefore making it possible to optimization the foam and complete sandwich composite with a reduced number of trials.

The third research objective is to optimize the polyurethane process using a surrogate part, (automotive truck tonneau cover) with and without the presence of the fibreglass reinforcement. The goal is to optimize the thermal and mechanical properties of the foam and the resulting sandwich structure.

This research project will serve to define the capabilities and limitations of this new technology. This study will open the scope of this novel process and bring a scientific knowledge of the complex behaviour of resin foaming and fibre impregnation.

1.2 Overview of Sandwich Composites

A sandwich composite is made by combining fibre reinforced skins with a low density core. The objective of the core is to increase the thickness of the section while reducing the overall weight of the structure. The resulting sandwich material will therefore exhibit a high specific stiffness and high strength, as understood; the stiffness of the structure is proportional to the square of its thickness. This serves designers in many ways, in some instances the sandwich composites are used for purely structural reasons where reduced weight is the goal, as well as for imparting enhanced properties such as vibration and noise damping, improved insulation behaviour and impact resistance. Additionally sandwich composites can influence the fatigue behaviour of the composite as discovered by Zabihpoor et al. Where four distinct damage events were found, two of them propagating from the foam core resulting in higher load ratios [7].

One of the current problems facing aeronautical composites today with the introduction of carbon fibre composites is the increase in vibration, noise transmission and electrical conductivity of the fibres. In the near future sandwich composites may serve designers in resolving some of these material behaviour issues.

Use of sandwich composites is increasing in both the aeronautical and automotive sectors [8]. The constituent materials include reinforcing fibres, resin matrix, core material, and possibly thermoplastic facing skins. As with typical composite structures the fibres are the major load carrying component, the matrix aids in transferring the stress between the fibres and the core. As well, the core is used to increase the thickness and flexural stiffness of the composites. Ideally, the core should be as light as possible. However, in order for the core to transmit the forces through the sandwich structure, it must not yield when encountering the tensile and compressive forces. The surface skins are typically used to impart cosmetic qualities to the part; as well as specific environmental properties such as chemical resistance, temperature resistance and flammability resistance.

1.3 Constituent Materials

There are typically four constituent materials for sandwich composites: the polymer matrix, the reinforcing fibres, the core and the surface skins. The polymer matrix can be either thermoplastic or thermoset. In some cases the polymer matrix and the core are the same polymeric material.

Thermoset matrices dominate the sandwich composite market. There are many core materials to choose from, honeycomb structures made with either aluminum, Kevlar or polyimide, foams made from polyurethane and thermoplastic materials, low density wood products such as Balsa, and syntactic foams made by combining epoxy or phenolic matrices with hollow glass bubbles. The surface skins are often made with thermoplastic materials because of their thermoformability and ability to impart characteristics such as, colour and texture. Thermoset skin materials are also used; as well as, but less common, thin metallic skins, typically aluminum.

1.3.1 Matrix

Composite materials can be classified into three groups depending on their matrix: polymeric, metallic and ceramic. Figure 1-9 illustrates the versatility and numerous possibilities for composites. The focus of this research is to develop composites made with polymer foams, specifically polyurethane foam sandwich structures.

The roll of the matrix in the composite is to protect the reinforcing fibres from damage, aid in transferring the loads from the fibres and aid in shaping the part. The selection of the matrix material is critical depending on the final use environment. If extremely high service temperatures are required the matrix materials are generally ceramic where as for low temperature applications under 200°C polymeric matrix materials are common.

In the polymeric family there are two sub families: thermoplastic and thermoset. Thermoplastic matrix composites are processed by heating or softening the resin followed by forming and then cooling. A common difficulty producing composites with a thermoplastic matrix is managing the high viscosity of the matrix which can be 1000 times higher than the viscosity of a thermoset matrix. The increased viscosity increases the difficulty of wetting out the reinforcing fibres. In order to manufacture thermoplastic composites, high pressure tooling and injection equipment are required, as well as high temperature moulding conditions. There have been some advances in this area using comingled reinforcing fibres with thermoplastic fibres. This reduces the distance the thermoplastic matrix must flow in order to wet out the fibres. Therefore reducing the processing pressures needed to form the material.

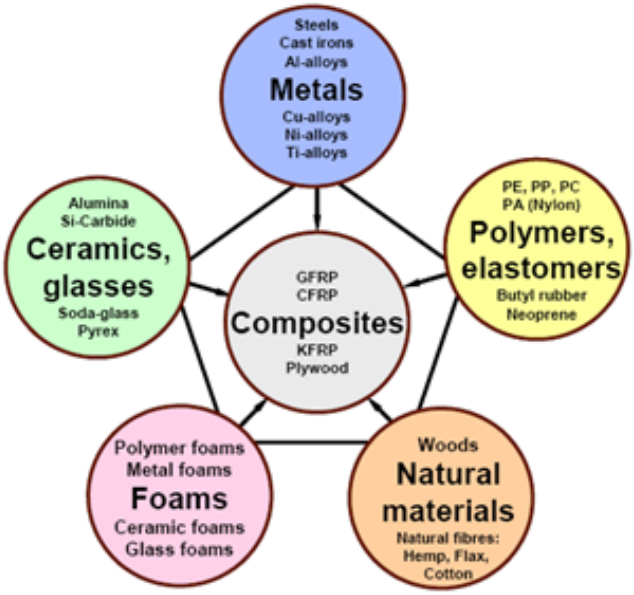


Figure 1-9: Material selection chart for composites [9].

Thermoset polymers are very common in the composite manufacturing industry. Low viscosity monomers can be combined with catalysts or reacting intermediates. An irreversible reaction is initiated where the molecular weight of the polymer begins to increase. During this reaction, the viscosity of the polymer increases eventually turning into a solid material. Thermoset materials retain their shape when heated but eventually begin to lose their properties when exceeding their glass transition temperatures. Thermoset resins have a number of advantages over thermoplastics. There is a wide spectrum of thermoset resins to choose from and their mechanical properties can be manipulated easily according to end use environments. The most common thermosetting resins used today include: polyurethanes, epoxies, polyester and vinyl-esters. Table 1-1 illustrates the advantages and disadvantages of these families of thermoset resins.

Table 1-1: Advantages and disadvantages of thermoset resins.

Thermoset Resin	Advantages	Disadvantages
Polyurethane	Ability to engineer properties, mid level mechanical properties, rapid reaction, low cost, no or low VOC's	Post cure required to achieve properties, critical mixing proportions, high chemical toxicity, water absorption

Epoxy	Ability to engineer properties, high mechanical and thermal properties, high water resistance, low cure shrinkage, low VOC's	Critical mixing, corrosive handling, generally slow reactivity, high cost
Vinyl-ester	Mid level mechanical properties, high chemical and environmental resistance, can use low profile additives (LPA's) to reduce shrinkage, medium cost	Post cure generally required, high styrene content, LPA's increase costs, high VOC's
Polyester	Low viscosity, ease of use, can use LPA's to reduce shrinkage, low cost	Low level mechanical and thermal properties, high styrene content, high cure shrinkage without LPA'S, LPA'S increase costs , high VOC's

In order to choose the right matrix material for a given application, the thermal and mechanical properties must be understood. Table 1-2 shows the typical properties of these thermoset matrices.

Table 1-2: Matrix properties for common materials [10].

Matrix	Density (g/cc)	Tensile strength (MPa)	Tensile modulus (GPa)	Coefficient of thermal expansion (10^{-6}m/m/°C)	Glass transition temperature (°C)	Cure shrinkage (%)
Epoxy	1.2-1.3	55-130	2.75-4.1	50-80	Up to 330	1-5
Vinyl-ester	1.12-1.32	73-81	3-3.5		Up to 120	5-7
Polyester	1.1-1.43	34.5-103	2.1-3.45		Up to 100	5-10

1.3.2 Reinforcing Fibres

The purpose of the fibres in a structural composite is to support the structural loads. There are many types of fibres used in industry: Carbon, Aramid, Basalt and natural fibres. The properties of common fibres are listed in Table 1-3.

Table 1-3: Typical properties for common fibres [10].

Fibre	Typical diameter (μM)	Density, (g/cm^3)	Tensile Modulus (GPa)	Tensile Strength (GPa)	Strain to failure (%)	Coeff. of thermal expansion (10^{-6}/m/°C)
Carbon, PAN T300	3	1.78	231	3.65	1.4	-0.6 longitudinal 7-12 radial
E-Glass	10	2.55	72.4	3.45	4.8	5
S-Glass	7	2.49	86.9	4.3	5	2.9

The use of fibres in a composite imparts unique material behaviour. One of the key differences and advantages using composite materials over isotropic materials like metals and plastic is the ability to create an anisotropic structure with engineered properties. In a simple case where unidirectional fibres are used as shown (see Figure 1-10), the properties of the composite are governed by Hooke's law. Assuming a perfect bond between the fibres and the matrix, the strain in the composite will be equal for the fibres and the matrix:

$$\varepsilon_{composite} = \varepsilon_{fibres} = \varepsilon_{matrix} \quad (1\text{-}1)$$

The stress (σ) carried by the fibres and the matrix can be calculated from the relationship between strain (ε) and tensile modulus (E) as shown in the following equations:

$$\sigma_{fibres} = E_{fibres} \times \varepsilon_{fibres} = E_{fibres} \times \varepsilon_{composite} \quad (1\text{-}2)$$

$$\sigma_{matrix} = E_{matrix} \times \varepsilon_{fibres} = E_{matrix} \times \varepsilon_{composite} \quad (1\text{-}3)$$

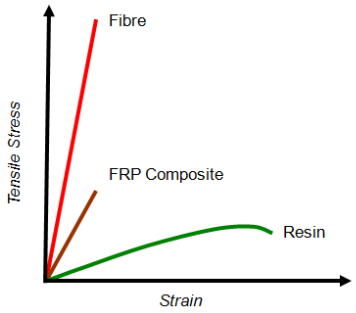
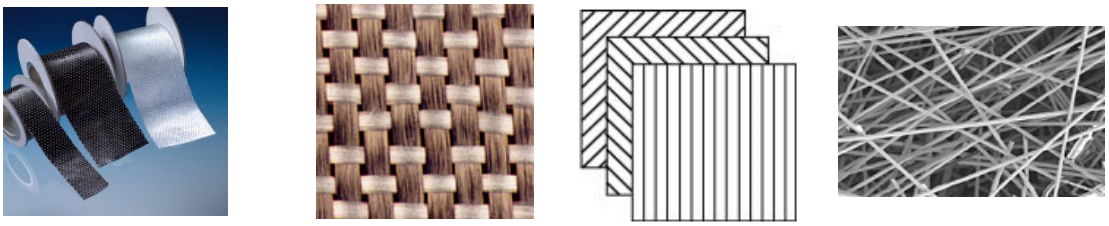


Figure 1-10: Tensile stress versus strain in a FRP composite [9].

Since the tensile modulus of the fibres is 100 times higher than the resin, most of the stress in the structure will be taken by the fibres. It can then be concluded that to fabricate high performance composites the orientation of the reinforcing fibres must be well controlled. Commonly for liquid moulding, the fibres are first converted into textile fabrics using different weaving and stitching systems. The weave patterns have been developed for various purposes: to achieve high fibre volume fractions, to facilitate draping and forming, to enhance fibre wetting and to reduce waviness on the surface, to maximize mechanical performance and to reduce warpage after curing. The style of the fabric can be classified into four categories as shown in Figure 1-11.



a) Unidirectional tapes

b) Weaves or knits, 0/90° or +-45°

c) Multiaxial layered fabrics

d) Chopped or continuous strand fibres

Figure 1-11: Common fibre arrangements used to make composite parts[9].

Within the category of weaves and knits there are many styles of fabrics as shown in Figure 1-12.

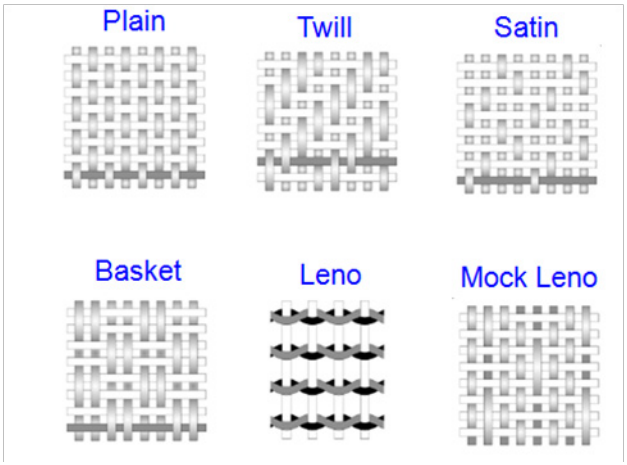


Figure 1-12: Common types of woven fabrics [9].

The satin style fabrics are used to minimize fibre printing while maximizing stiffness. Knitted fabrics are also very common; these are similar to unidirectional tapes where the fibres toes are kept straight. Stitches are used to lock the fibres at the warp 0° direction and weft 90° direction. There are a few advantages using stitched fabrics over wovens; the processing is faster therefore their cost by areal weight is lower. Also, because the fibre toes are straight instead of crimped their tensile properties are higher than for woven fabrics. However, woven fabrics have better draping characteristics and out of plane properties. The orientation of the toes and the location of the interlocking stitches are shown in Figure 1-13.

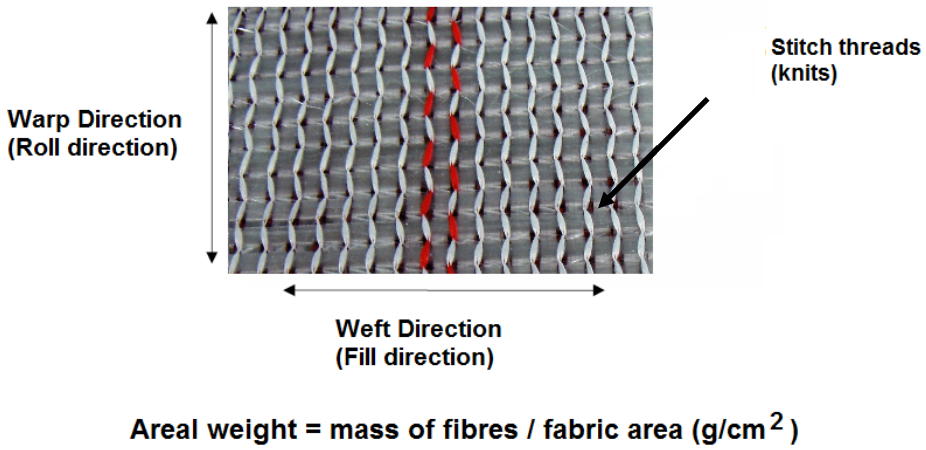


Figure 1-13: 0-90° stitched fabric.

1.3.3 Outer skins of sandwich composites

The primary purpose of the skins in a sandwich composite is to impart cosmetic appearance for the composite (see Figure 1-14). When engineered fabrics are used to fabricate composites, a phenomenon known as fibre printing may occur. Differential shrinkage between resin rich and fibre rich areas generate waviness in the part surface.

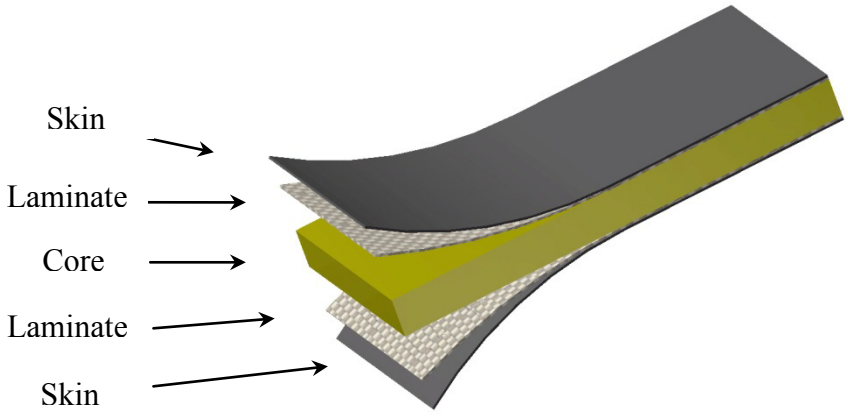


Figure 1-14 : Schematic of a sandwich composite.

This is generally more severe between the toes as illustrated in Figure 1-15. The final result can be a wavy surface on the finished composite part.

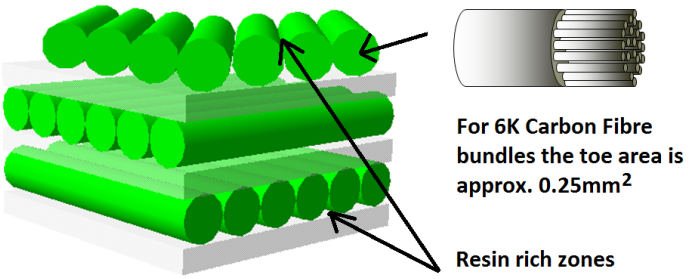


Figure 1-15: Representation of composite laminate with fibre and resin rich zones.

Surface skins are used to improve the surface finish of these composites. Polyester or vinyl-ester Gelcoats are widely used for this purpose. These materials are sprayed directly on the mould surface acting as a barrier and are made with similar polyester or vinyl-ester resins with an additive package targeting the desired surface properties. Some additives include; high levels of inorganic fillers ($CaCo_3$, Aluminum Trihydrate), low profile additives, ultraviolet resistant additives and impact toughenners. Gelcoat films are created by applying a thin coat directly on the mould surface using a spray gun. The Gelcoat will first turn from a liquid to a semi-cured solid. When tacky to the touch, the fibre preform can be placed on top of the Gelcoat, followed by closing the mould and injecting the resin. Timing the exposure and onset of curing between the two reacting polymeric materials can increase the chemical bond between the skin and matrix resulting in improved mechanical performance. The down side using Gelcoats is the release of high levels of Styrene during spray application and during open mould curing. There have been efforts to reduce emissions as described in the EPA report EPA/600/SR-97/018 but these only reduce the styrene emissions not eliminate them [11].

Additional issues encountered using sprayed skins include cracking at demould and the creation of defects due to variable thickness of the skin.

Another material used to form spray skins is a polyurethane-derived, ultra fast curing polyurea. Similar to Gelcoats, there is a wide window for formulating engineered properties with this material. Polyurea coatings are in the elastomer family and can be made with either aromatic or aliphatic isocyanates. In general, polyurea skins offer increased toughness and good chemical resistance. In order to achieve UV stability, aliphatic isocyanates can be employed. Suppliers of these materials include Bayer Material Science, Dow Chemical and Recticel Ltd. There are advantages with polyurea skins when using PUR based cores. Specifically, there is increased

compatibility between the two materials resulting in improved interface properties. Draw backs with polyurea spray systems include the requirement of precise high pressure metering equipment and the requirement for additional environmental controls due to the high toxicity of atomized amines and isocyanates.

Pre-moulded thermoplastic skins are also commonly used to protect composite parts. The desired material properties can be engineered into the thermoplastic to impart UV resistance, thermal resistance, colour, impact resistance, chemical resistance, texture as well as electrical insulation. To create the skin, typically a thin film is produced with the desired thermoplastic composition. Depending on the application the skin can be either monolithic or a more complex multi-component structure. After the film is formed it can be thermoformed into the desired part shape. The 3D skin is then inserted directly into the composite mould. Special care must be taken to account for differential thermal expansion and shrinkage during the moulding stage. There are many advantages using thermoplastic skins which include the elimination of post painting, resulting in a significant reduction in the release of VOC's. There are however some limitations to this technology, such as warpage due to differential thermal expansion, delamination or creation of bubbles between the composite and the skin, possibility of cracks and temperature limitations.

Pre-preg films made using partially cured B-stage epoxy films can also be used to make skins for epoxy composites. The pre-preg films are produced in either sheet form or they are stored on rolls. Depending on the end use temperature and environment, there is a wide variety of matrix materials to choose from, such as epoxies, phenolics, bismaleimide and polyimide's [12]. These films must be kept frozen until the beginning of the moulding stage. The reduced temperatures are necessary to prevent the B-staged materials from curing or aging before use. There is a wide variety of techniques used to form these films. Most common is to use a numerically controlled cutting table to pre-cut the patterns, followed by manual placement or vision guided placement on the mould. Preforming is usually done by hand or with the aid of vacuum films. Curing can be accomplished either in-situ with the composite fabrication or separately.

Lastly, metallic sheets can also be used as skins for composite parts. Aluminum facing skins are often used with thermoplastic honeycomb cores or moulded PUR cores. Aluminum foil skins are typically 0.5 to 1 mm thick; however there are manufacturers who are producing aluminum face

sheet composites with foils as thin as 0.026 mm [13]. The support provided to the thin Aluminum film from the core or polymeric composite makes it possible to reduce the thickness of the Aluminum, while providing damage protection to the part.

1.4 Sandwich Materials

The primary use of the core is to increase the rigidity to the composite while minimizing its weight. The general term for bending stiffness is flexural rigidity (D), which is the product of the material elastic modulus (E) and the cross section moment of inertia (I), so for a symmetric sandwich beam where the two facing skins have the same properties, the following equation applies [14] (see also Figure 1-16):

$$D = EI = \frac{E^f bt^3}{6} + \frac{E^f btd^2}{2} + \frac{E^c bc^3}{12} \tag{1-4}$$

Where: E^f = Elastic modulus of the facings

E^C = Elastic modulus of the core

b = Width of the beam

d = distance between facing centroids

t = thickness of a facing

c = Core thickness

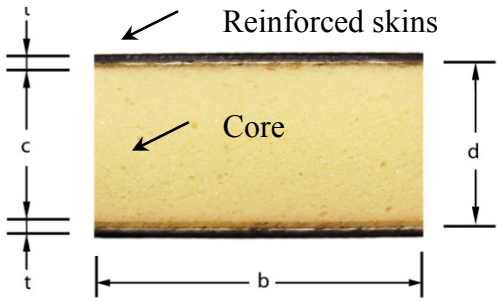


Figure 1-16 : Schematic of a sandwich composite.

Equation (1-4) can be simplified if the skins are relatively thin compared to the core (d/t > 6) and the core material is considerably weaker than the skins, then it can be reduced to:

$$(E^f/E^c) \cdot xtd^2 \tag{1-5}$$

$$D = EI = (E^f btd^2)/2 \tag{1-6}$$

From equation (1-6), it is observed that the core material does not directly contribute to the stiffness (for the low density core case). Therefore, it is advantageous to concentrate the reinforcing fibres near the facing which will act like an 'I' beam increasing the rigidity of the

part. Researchers at Queen's University Kingston, ON, recently published a work "Structural Performance of Sandwich Wall Panels with Different Foam Core Densities in One-way bending" discovering that by increasing the density of the foam core in the sandwich composite the flexural stiffness of the panels increased significantly challenging the simplification represented in Equation (1-6) [15].

The schematic representation of a PUR sandwich composite (PFSC) is shown in Figure 1-17. The function of the core is then to separate the facing materials until the desired stiffness is achieved. The core will also transmit the forces though the composite and between the skins, therefore the shear properties of the core will have a significant effect on the final sandwich composite.

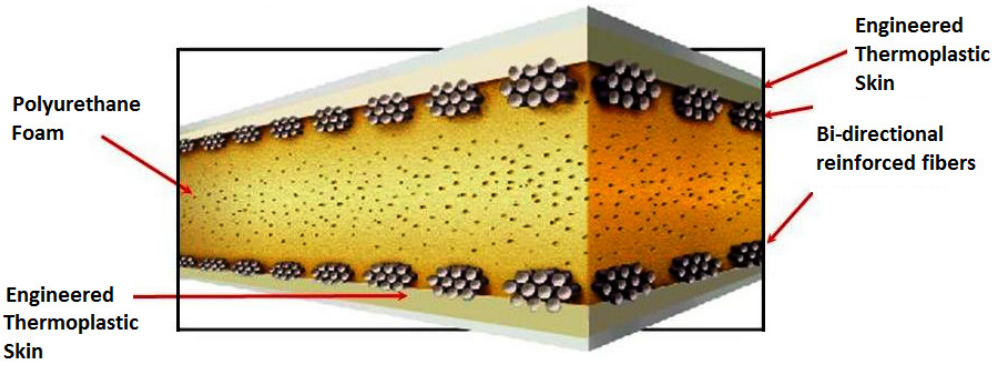


Figure 1-17: Schematic of the Poly-Foam Sandwich Composite (PFSC) [6].

There are many different core materials used to make sandwich composites from thermoplastic to thermoset polymers. Some commonly used cores include: Polyvinyl Chloride foams (PVC), Polyester foams, Poly-Ethylene-Terephthalate (PET), and Styrene Acrylonitrile (SAN). One advantage of the thermoplastic foams is their thermoformability. There are also several thermoset foams cores, made using polyurethane foams (PUR), polyisocyanurate foams (PIR) and syntactic epoxy foams. Thermoset foam cores offer more versatility than thermoplastics, superior properties and they are easier to mould into 3D shapes. There is also a family of honeycomb structures made using Kevlar paper impregnated with phenolic resin under the trade name of Nomex®. Also Aluminum honeycomb materials are used to make sandwich composites. The honeycomb structures are lighter in weight and typically have superior properties than foams [14]. The last type of core material used is Balsa wood. These ecological friendly cores offer

good mechanical properties. However their weight can be high and they have poor water resistant properties. Examples of some commonly used cores are shown in Figure 1-18.

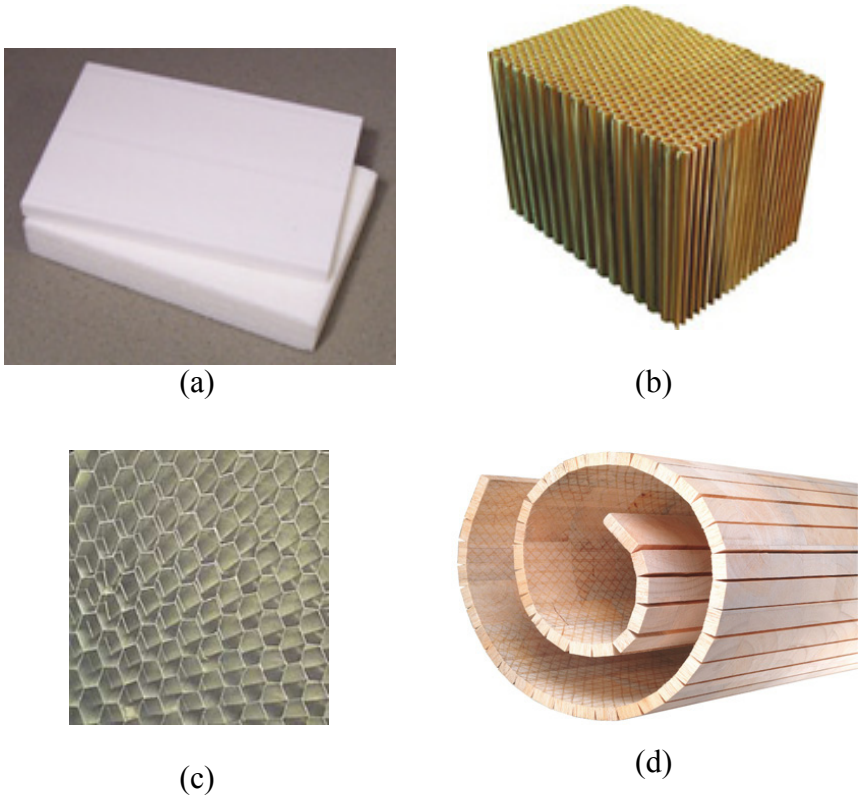


Figure 1-18: Common core materials used to make composite parts: (a) thermoplastic (SAN) foam, (b) Nomex® honeycomb [16], (c) Aluminum honeycomb, and (d) Balsa wood [17].

In the aerospace sector, Nomex and aluminum are the most commonly used core materials. In the automotive industry polyurethane cores are common and in the recreation industry end grained Balsa wood and thermoplastic cores are frequently used.

1.4.1 Advantages of polyurethane sandwich structures

Polyurethane (PUR) and polyisocyanurate (PIR) foams are commonly used in sandwich structures. PUR and PIR are formed when reacting monomers with at least two alcohol groups (OH) with monomers with at least two isocyanate functional groups (NCO) in the presence of a catalyst. The formation of these materials does not result in the release of styrene compounds or other VOC's which are under environmental restrictions. Polyvinyl chloride (PVC) and styrene acrylonitrile (SAN) foams fall into this category of undesirable products due to use of styrene and chlorine which are both under stringent EPA regulations [18].

Another advantage using PUR and PIR is the ability to modify the material chemical structure and resulting mechanical and thermal properties. As a result, these materials offer a wide range of hardness, density, and stiffness.

There are also several moulding methods for PUR and PIR foams, such as, reaction injection moulding (RIM), continuous in-line lamination, continuous slab foaming and box foaming. One of the biggest advantages of these foams is in the ability to mould complex net-shape cores, reducing scrap material and multiple machining and forming operations.

Compared to other thermosetting foaming materials such as syntactic foams (epoxy), PUR foams react and cure quickly. Cure times are dependent on thickness and density; however, in most cases the PUR materials can be demoulded in minutes; from 8 to 20, where most epoxy syntactic systems can take hours to cure.

1.4.2 Limitations of polyurethane sandwich structures

PUR and PIR foams although extremely versatile, require a significant capital investment to set-up a moulding unit. A typical line would consist of a roboticized dispensing unit, line conveyor, curing oven, mould opening and closing station, cleaning and waxing area and a place to insert components. This capital investment often requires high volume manufacturing, which is why these materials are commonly used in the automotive industry.

The PUR and PIR foam formulations have good compression strength and moderate physical properties at higher densities, but low density foams have a tendency to be friable; with low abrasion resistance and relatively low fatigue life. In the marine industry, higher density less friable versions of these foams are used extensively in transoms, due to their high compressive strength, while the lower density materials are used in stringers [16,17].

The high reaction speed for PUR and PIR foams can lead to some difficulties processing these materials. In the case of SRIM where PUR is injected through a fibre preform, two problems are encountered; first the high initial viscosity of PUR results in difficulty permeating the fibre preform. The initial PUR resin viscosities range from 1000 to 2000 cps. Second, due to a rapid increase in viscosity due to polymerization, fibre wetting becomes very limited. As a result SRIM manufacturing has not seen an important growth in the industry.

CHAPTER 2 REVIEW OF SANDWICH COMPOSITE MANUFACTURING PROCESSES

2.1 Introduction

This chapter presents some of the different manufacturing processes used to make composite parts based on polymer matrix and ceramic fibres. The processes described can be used to make sandwich parts with and without polymeric core inserts.

2.1.1 Hand wet lay-up process

One of the most common methods used to make composite parts consists of a manual labour process called hand wet layup. In this process, first a surface coat is applied to the mould, next the dry fibres are placed on the mould, and finally the fibres are manually impregnated with resin using rollers (see Figure 2-1). The core, often made from thermoplastic foam, is then placed in the mould. A second layer of dry fibres are placed on top of the foam and manually impregnated with resin. The part is then cured for a few hours and demoulded.

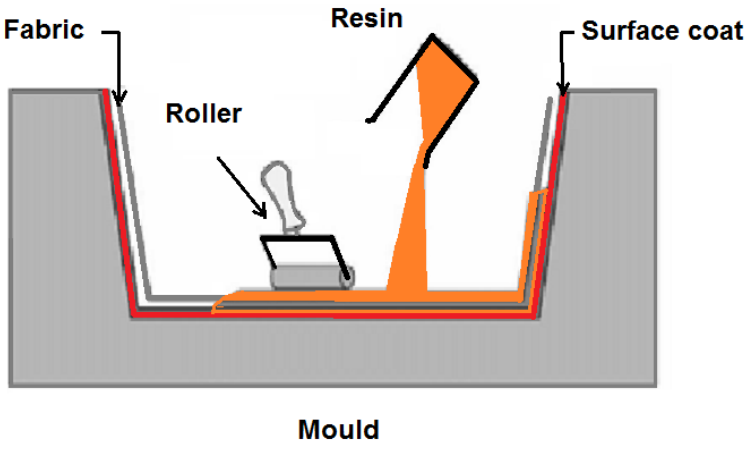


Figure 2-1: Hand wet layup process [19].

This process requires a high degree of hand labour and is limited to very low production volumes. Also use of this process is avoided where possible because of worker exposure to toxic chemicals and fibres, as well as the release of high quantities of volatile organic compounds (VOC's) [11]. Finally, mechanical properties are often inconsistent between parts due to the hand dependence on fibre compaction.

2.1.2 Vacuum Assisted Resin Infusion (VARI)

The main advantage of this manufacturing process is that it requires only a single sided mould. In VARI, resin impregnation of the fibres is accomplished using a differential pressure created using a vacuum pump and a vacuum film. A schematic of the VARI process is shown in Figure 2-2. If cores are used they are placed between the laminate layers. To facilitate resin impregnation, the cores can have slits machined into the surface to act as resin channels. Also, holes can be drilled through the core to facilitate resin flow between faced reinforcing layers.

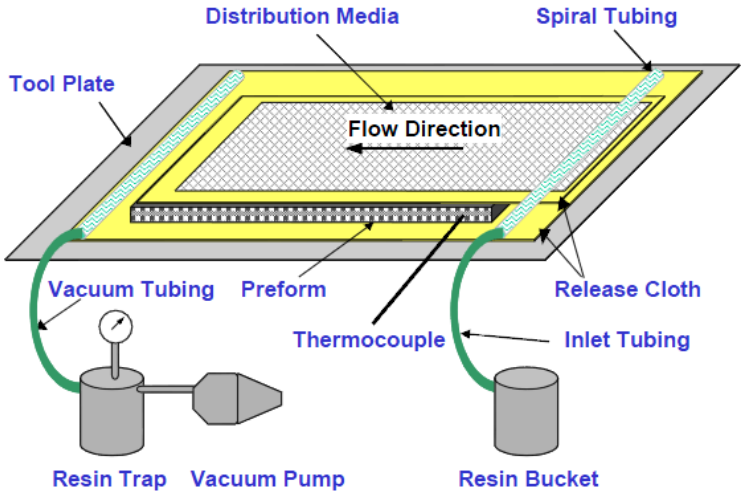


Figure 2-2: VARI process schematic [20].

The VARI process is widely used to fabricate large composite parts. Although the process is relatively simple, it is difficult to automate and requires a large quantity of consumable materials such as vacuum bag film, distribution media and peel ply. Also, because there is only one atmosphere of vacuum pressure, the compaction of the fibres is very limited resulting in low fibre volume contents (V_f).

2.1.3 Compression moulding using the LFI-PUR®-Technology

Long fibre injection (LFI) is a process developed by Krauss Maffei Corp. This rapid PUR process consists of injecting long and short chopped glass fibres, directly into the resin stream in a high pressure polyurethane mix-head. By introducing the fibres directly into the stream of the PUR resin, improved wetting of the fibres results. Direct injection into a closed mould is not possible with this system, robots are used to pour or lay down the mixture of fibres and resin in open

moulds as shown in Figure 2-6. An advantage of the LFI process is the elimination of the fibre preform shown in Figure 2-4; here low cost roving's used instead as shown in Figure 2-3. The novelty of this process lies in the mix-head where the fibres are introduced into the resin stream shown in Figures 2-5 and 2-6 [21].

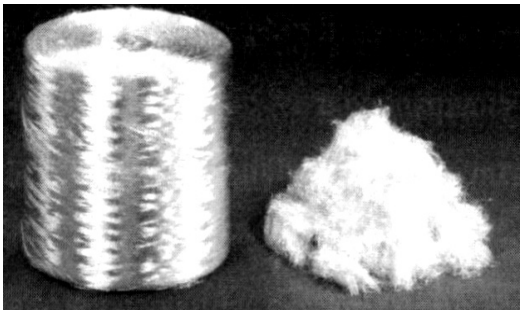


Figure 2-3: Low cost fibre roving's.

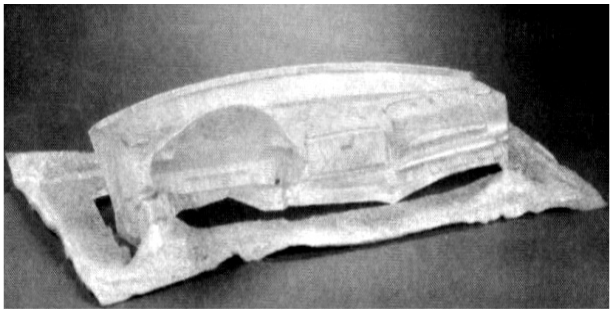


Figure 2-4 : Example of a preform.

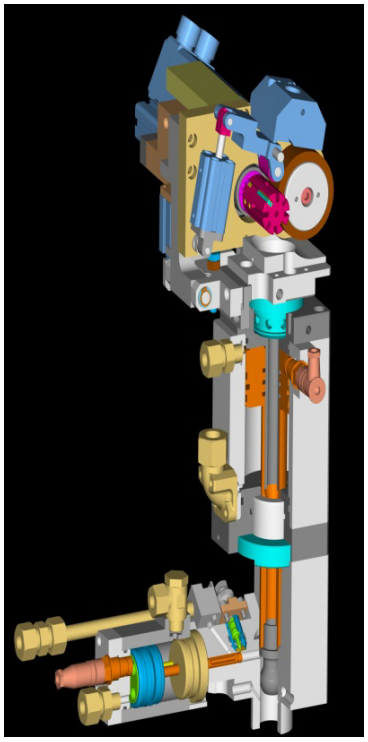


Figure 2-5: Schematic of LFI mix-head [21].

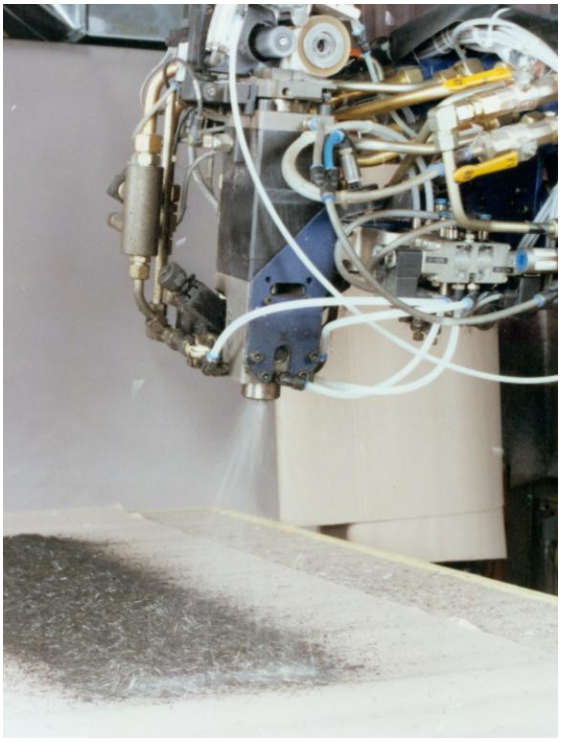


Figure 2-6: LFI mix-head in operation [21] .

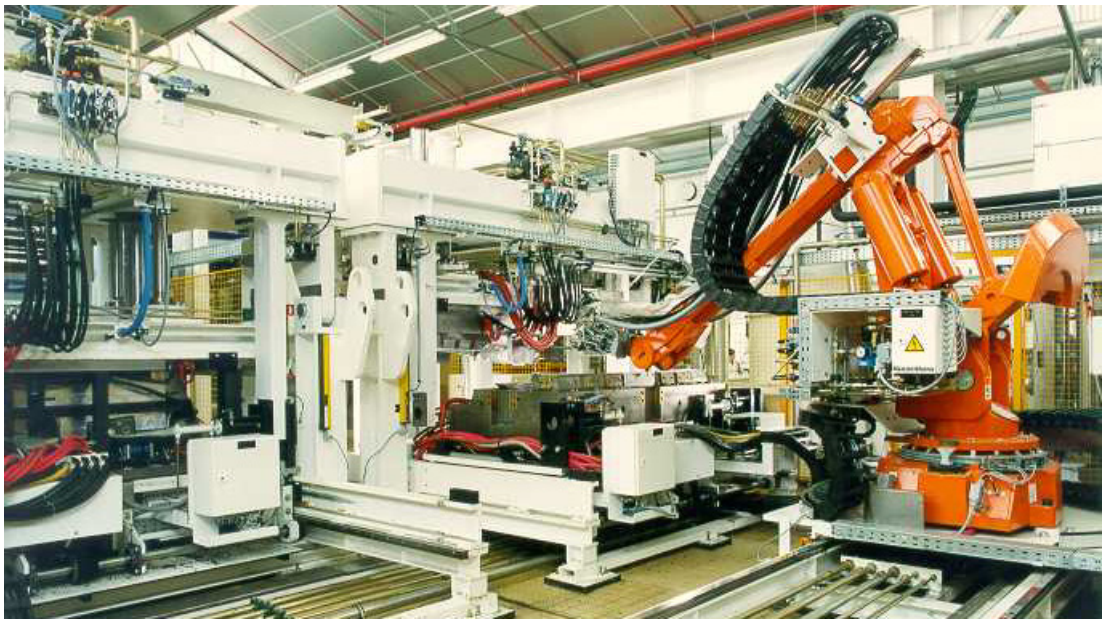


Figure 2-7: Linear automated LFI work cell [21].

There are some limitations with this process; first, because of the randomly placed chopped fibres the mechanical properties are limited. Second when moulding foamed structures, the fibre distribution is random throughout the thickness of the part resulting in lower flexural rigidity and increased weight compared to sandwich structures where the reinforcement is located next to the facing skin, lastly, this process is capital intensive, automation cells can cost in excess of $5,000,000 making equipment amortization costly.

2.1.4 Compression moulding using the Baypreg® Composite Process

The Bayer Corporation has developed a unique composite moulding process utilizing a urethane spray system that applies liquid PUR resin directly onto corrugated aluminum or cardboard preforms with fibreglass facing layers. A US patent was issued to the Bayer Material Science AG. in 2008, Wilkens et al. [22].

After a controlled amount the Baypreg PUR resin is sprayed on both sides of the preform, it is then transferred into a rigid mould, followed by closing under pressure. A schematic of the process is depicted in Figure 2-8 showing 1) the robotized preform cutting and load cell, 2) the PUR spray unit, 3) the placement of the impregnated preform on the open mould, 4) the mould closing and part curing cell, 5) the demoulding station and 6) the finalized part. This low pressure compression moulding process results in the rapid production of composite sandwich

parts. This process is capable of producing parts in less than two minutes. The limitations of this process include: poor surface finish quality which has prevented this process from being used for exterior "Class A" parts, and low mechanical properties due to low fibre volume contents (V_f), and when using the cardboard cores moisture ingression can limit use to dry applications. Figure 2-9 shows an example of an automotive interior part produced by this technique.

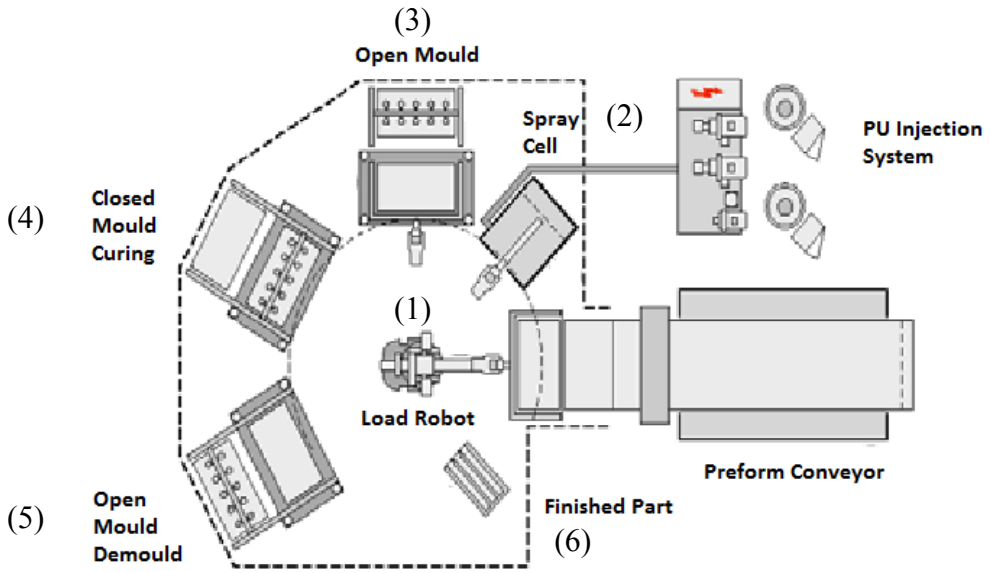


Figure 2-8: Baypreg F Nafpur Tech™ Technology work cell [23] .

Figure 2-9: Baypreg F load floor for the Audi A4 [23].

2.2 Overview of Poly-Foam Sandwich Composite Process (PFSC)

The proposed multi step process is a convergence of many technologies; thermoforming to form the inner and outer skins, vacuum pre-forming to shape the reinforcing fabrics, UV curing to

rapidly bond the fabrics to the thermoplastic skin, RIM injection to create the core, wet out the fibres and bond to the skins. The result is a three dimensional (3D) sandwich structure. The process is illustrated in Figure 2-10 from thermoforming, preforming, PUR injection to final assembly.

Figure 2-10: Process flow for the Poly-Foam (PFSC) process.

2.2.1 Fabrication of the thermoplastic skins

The thermoplastic skins are manufactured in two distinct steps. First a thermoplastic sheet is extruded by traditional means, and then the sheet is thermoformed into the final part dimensions. The two steps are described in the following sections.

2.2.1.1 Thermoplastic sheet extrusion

Plastic extrusion using roll dies is a technique used to make custom flat plastic sheets at controlled thicknesses from formulated resins. With advanced extruders up to seven distinct layers can be extruded at the same time; creating monolithic or multi-axial sheets with engineered

properties. The formulated resin pellets are loaded into the single or multi screw extruder where they are gradually heated, the molten plastic is later injected into a trough in front of the parallel steel rolls. Flooding the trough with molten resin creates a resin bank in front of the roll. The molten resin passes through the rolls which have a pre-set gap. The hot sheet then passes to the first take off unit. The process continues and the sheet passes to the second take off unit where it is cut to length. Shown below in Figure 2-11 is the schematic representation for this process provided by the Qingdao Xindacheng Plastics Machinery Company. In many cases the multi-axial sheets are needed to impart the properties for the final part. For example if UV resistance is required a thin cap layer can be extruded using Poly(methyl methacrylate) (PMMA) or a layer of Acrylic Styrene Acrylonitrile (ASA). Depending on the service temperature for the final part, ABS or blends of PC/ABS can be used in the core of the sheet, and finally if increased chemical resistance is required on the inner surface, a thin layer of Polybutylene Terephthalate (PBT) can be extruded in situ. An alternate method for creating a multi layer sheet involves calendaring pre-extruded films during the extrusion process. This is sometimes necessary if the melt points for the different resins are too far apart and if there are compatibility issues with the resins.

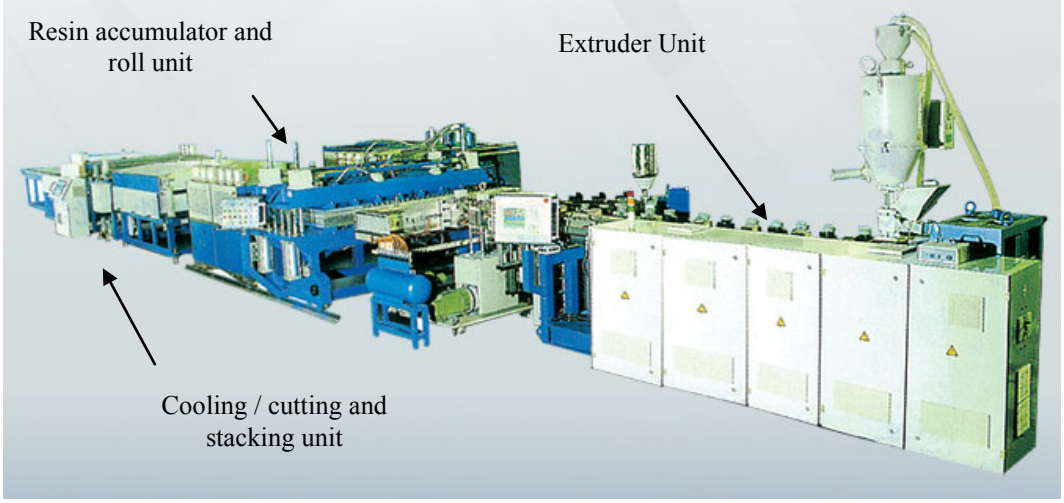


Figure 2-11: Sheet extrusion process overview [24]

2.2.1.2 Thermoforming the thermoplastic sheet

The flat thermoplastic sheet is then turned into a 3D part using the thermoforming process. A simple rotary thermoforming cycle is illustrated in Figure 2-12. First the flat sheet is loaded into the thermoforming machine, next the sheet transfers into the machines oven, when the correct temperature is reached the sheet transfers to the moulding area where a single sided mould is held

in a vertical press. The mould is closed and simultaneously vacuum is applied inside the mould. A vacuum box on the opposite side of the mould draws the air through small holes strategically located on the moulds surface. Simultaneously air pressure is applied to the opposite side of the sheet which aids in pressing the sheet into the mould. Within seconds the moulded part cools and begins to shrink away from the moulds surface. The mould then opens and the part is transferred to the demould station. The cycle time for a part using a plastic skin that is 1.2 mm thick is around 120 sec. An actual rotary pressure thermoforming machine is shown in Figure 2-13.

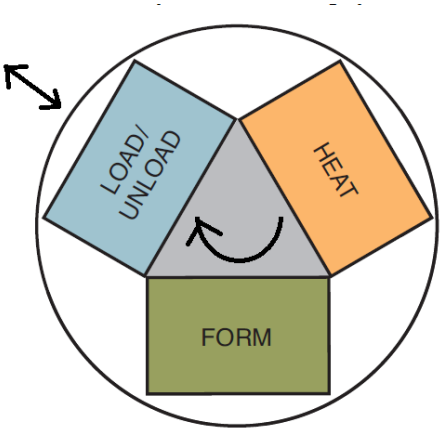


Figure 2-12: Process cycle for rotary thermoforming [25].

Figure 2-13: Brown® R-series pressure former [25].

The gage for the thermoplastic film is its starting thickness. Typically the thickness of the final part is developed based physical requirements; however, if the required thickness is lower than the minimum thermoformable thickness, a heavier gage sheet must be used. In practice the cost of the thermoplastic resin drives moulders to minimize the gauge of the film where possible. When deep or shallow parts are required the starting thickness of the sheet must be great enough prevent thinning and other defects when the sheet is formed. This is called the draw ratio for the part and this ratio is specific to the material being formed. Amorphous Acrylonitrile Butadiene Styrene (ABS) is one of the easier thermoplastics to form. Crystalline Polyolefin (TPO) thermoplastics have a narrower melting window compared to ABS and therefore increased difficulty when moulding.

The thermoforming process uses a single sided mould cavity in parallel with a pressure box. The moulds are often made using aluminum and are temperature controlled using integrated heating

lines. Depending on the thermoplastic used, the mould heaters typically use recirculating hot oil. The thermoforming moulding process is shown in Figure 2-14 [26]. As the mould closes the pressure box makes contact with the mould, air is removed from the cavity between the mould and sheet using vacuum. Simultaneously air pressure on the opposite side of the sheet assists in pressing the sheet to the mould. Baffles are used to distribute the air minimizing localized cooling.

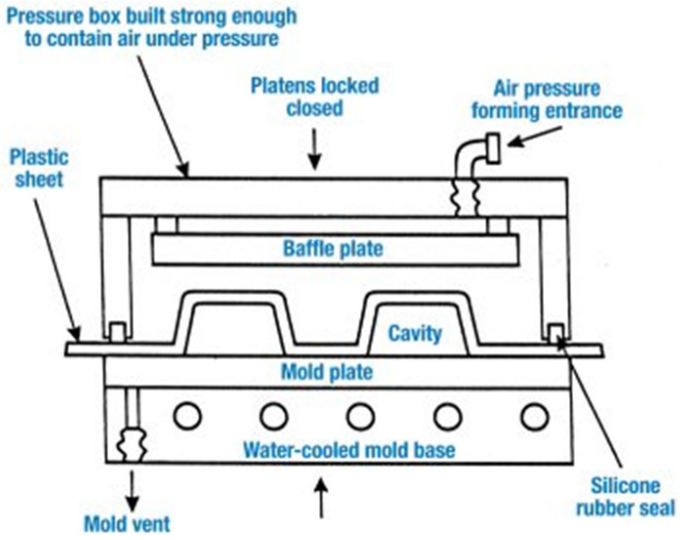


Figure 2-14: Thermoforming moulding process [26].

2.2.2 Fibre preforming & bonding

Fibre preforming is one of the enablers for this technology. When fabricating a sandwich composite precise location of the oriented fabric is necessary in order to achieve the desired properties. When thin light weight engineered fabrics are used with areal weights up to 800 g/m^2; it can be difficult to rigidize these materials using conventional preforming methods. And if the preform does not stay where desired in the mould during resin injection, defects will be uncontrollable and properties unpredictable. The following preforming concept was developed at Advance USA, where a multi functional thermoplastic skin would act as the holder of the glass fabric; making it possible to stitch bond the fibres to the inner surface of the skin precisely where needed in the composite. The thermoplastic skin can then be securely held in the mould using a vacuum force. The challenge now becomes how to bond the fibres to the 3D thermoplastic carrier sheet. Knowing there is a significant difference in the coefficient of thermal expansion between the thermoplastic and the inorganic fibre mat it is important that the bonding occurs at near

ambient temperatures. Ultraviolet curing is a logical choice for this problem. The adhesive binder can be applied to either the thermoplastic skin or the fibres. UV radiation can then rapidly cure the adhesive in seconds minimizing temperature increase.

2.2.2.1 Fabric cutting

The bi-directional stitched fabric can be cut to shape using a CNC fabric cutting table. These automated cutting systems reduce variation in the final part. Complex patterns can be cut easily and several layers can be cut at the same time. This type of equipment is necessary for production cutting and when preform repeatability is necessary. A Lectra V2500 was used to cut the patterns for this research project. The CNC fabric cutting machine is shown in Figure 2-15.

Figure 2-15: Lectra V2500 fabric cutting system.

2.2.2.2 Binder selection

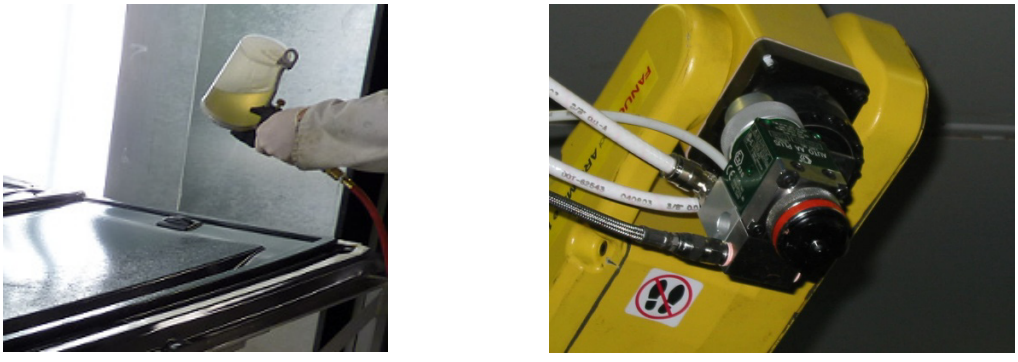
It is necessary to bond the fibreglass to the thermoplastic skins in order to be able to transport the skins to the mould and to prevent the fibres from falling into the cavity during injection of the PUR foam. The binder needs to bond well with both the fibres and the thermoplastic. It is important that the mechanical properties of the binder meet the needs of the composite to prevent negative interactions when subjected to environmental conditions such as high heat, therefore the binder should have similar properties to the PUR foam. In the case of an exterior component the binder will see temperatures up to 90°C; therefore, it is important that the binder can withstand the forces developed due the higher coefficient of linear thermal expansion (CLTE) of the thermoplastic skin. If the binder can't resist these forces delamination will occur at the interface of the laminate and thermoplastic skin. There is a second challenge when bonding fibreglass to a thermoplastic using a high temperature material. If the curing temperatures are high the

difference in CLTE between the fibres and binder will induce warpage in the skin which can lead to difficulties fitting the skins in the mould.

Taking all these considerations into effect, ultraviolet cured urethane acrylate oligomers are ideal for this application, due to the formulating versatility and the ability to keep the thermoplastic skin temperature down during the curing phase. This is due to the low exposure times necessary for curing UV reactive materials.

2.2.2.3 Binder application

There are many ways to apply the binder. Typically urethane acrylates are highly viscous up to 20,000 cps at room temperature. It is therefore necessary to have spray equipment that is capable of spraying highly viscous resin. The simplest method is to use a gravity feed Gelcoat sprayer shown in Figure 2-16(a). Although the UV binders are solvent free, it is desirable to spray automatically to improve repeatability and minimize operator exposure to airborne pollutants. A typical automated gun and robot are shown in Figure 2-16(b). To minimize the negative effect of the binder in the final composite it is desirable to minimize the quantity sprayed on the thermoplastic skin. This is done by applying a droplet like spray pattern with a high percentage of open space as shown in Figure 2-17. The binder's purpose is to hold the fibres close to the thermoplastic and to resist delamination from foam shear during injection. In fact the bond of the PUR to the thermoplastic is often much stronger than the UV binder again supporting the strategy of minimizing binder usage.



(a) (b)

Figure 2-16 : (a) Applying UV binder with manual gravity feed Gelcoat spray gun. (b) Automated Graco AA-Plus spray gun with a Fanuc robot [27].

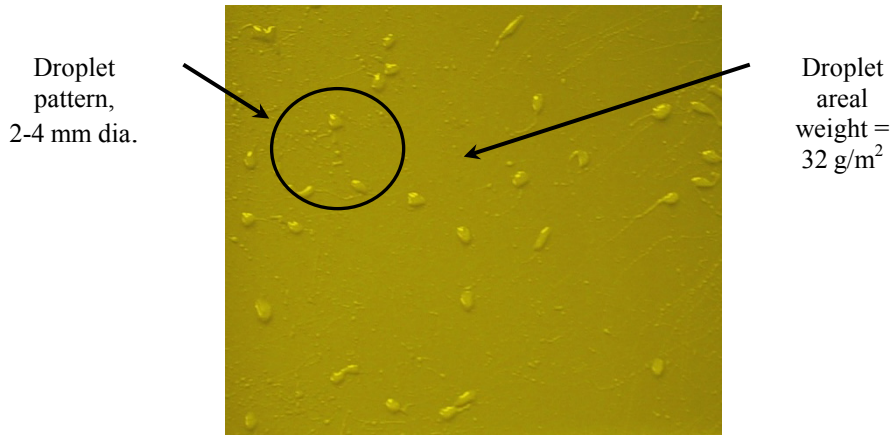


Figure 2-17 : Binder spray pattern and showing resin areal weight.

2.2.2.4 Binder curing using ultraviolet radiation

UV radiation is an ideal way to bond fibreglass to thermoplastic skins. It is possible to spray the binder on the thermoplastic skin followed by preforming. Using a clear polyethylene film the fibres can be consolidated using vacuum. The UV light can then be used to penetrate the film and fibreglass matt to cure the binder on the surface of the preform. The choice of UV initiator is important in developing a deep curing binder formulation. The UVV spectrum is ideal for this application. The typical lamp configuration is shown in Figure 2-18.

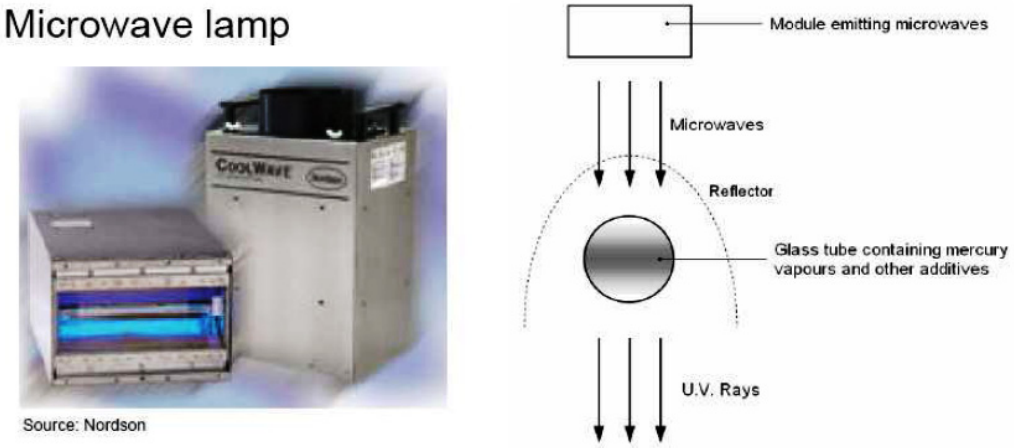


Figure 2-18 : Operating principal of UV lamps [28].

2.2.3 RIM Injection

The reaction injection moulding process (RIM) with PUR foam is challenging compared to other low pressure mixing LCM processes. PUR resins are often viscous and react extremely fast in seconds, compared to minutes or hours. It is therefore necessary to adequately mix the reactive components at precise proportions while at high flow rates. For example, when producing RIM foam it is necessary to inject the resin into the tool before the first polymerization of the foam starts. This minimizes the development of density gradients in the foam which look like waves in the part (see Figure 2-19). So if the desired part requires 50 kg of foam to fill the mould and the start of polymerization is around 12 seconds. It is advisable to inject all the resin in 10 seconds or at a flow rate of 5 kg/s. These rates are unheard of in traditional LCM moulding rates for polyester or epoxy resins where most systems peak out at around 0.6 kg/s.

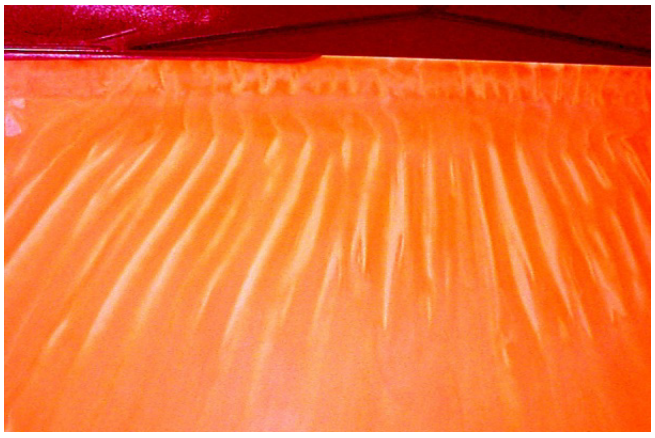


Figure 2-19 : Foam injection at flow rate of 500g/s illustrating density variations.

To achieve the required precision these injection systems require precision metering pumps and hydraulic mix-head opening valves. A schematic conceived by the author in 2007, for injecting epoxy using high pressure recirculation is shown in Figure 2-20.

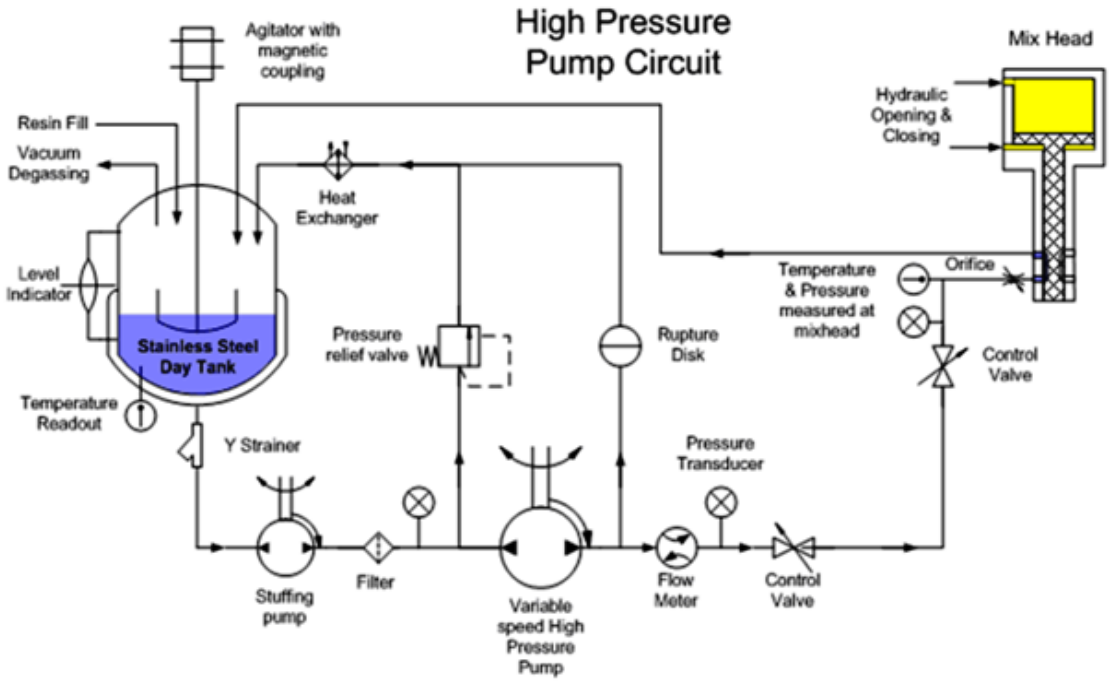


Figure 2-20 : Schematic representation of one side of a RIM metering machine.

The system works by recirculating the resin from a temperature controlled day tank to a mix-head mounted on the RIM mould. When the mix-head is closed it is possible to circulate the resin at the desired flow rate and pressure. Mixing occurs when the mix-head opens. The chemical components flow through orifices at pressures as high as 200 bars. The drop in pressure and inertial forces of the colliding streams induces the mixing. Static mixing elements are not required with impingement mixing heads. The impingement principal is shown in Figure 2-21. This new injection system was later designed and constructed by Robin Dubé, a fellow master's student at École Polytechnique under supervision of the author. This system is now being used by the CCHP laboratory LFIC located in St-Hubert QC.

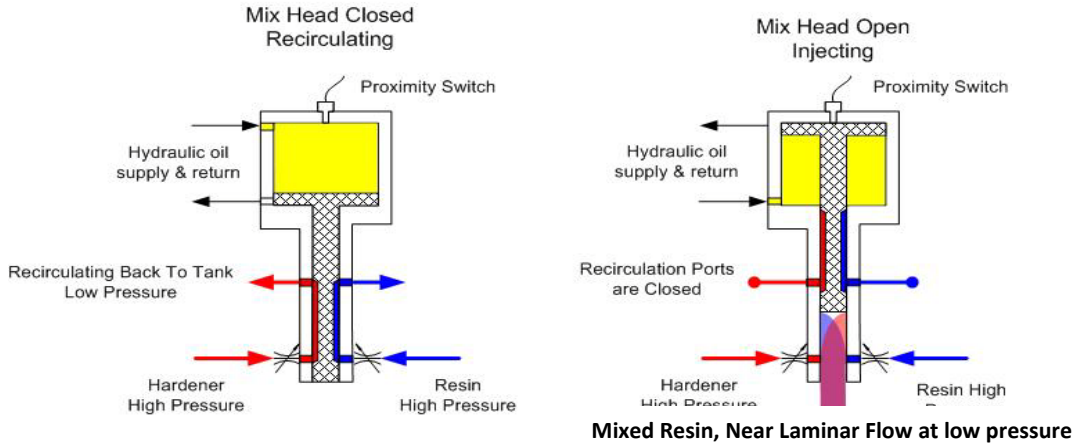


Figure 2-21 : High pressure impingement principal.

The complete RIM system with a mould is represented below in Figure 2-22. In this example, hydraulically driven cylinder pumps are used to meter the resin components. This is a common alternative to the high pressure piston pumps when the resins employ high levels of abrasive inorganic fillers.

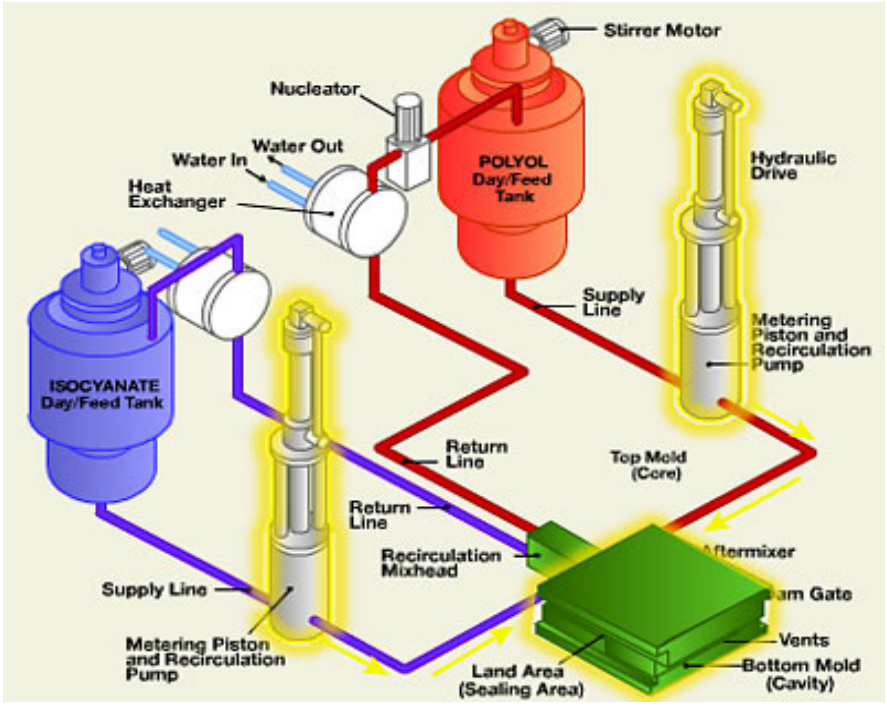


Figure 2-22 : RIM process by Henneke [9].

CHAPTER 3 PREFORM PROCESS DEVELOPMENT

3.1 Introduction to preform manufacturing methods

Preforming fibres for liquid composite moulding is one of the most challenging steps in producing a composite part. For high performance composites where fibre orientation is critical there are only a few processes that are production capable. Typically layers of dry fabric are cut and layered. The layers are held together using tackifiers, liquid resins, and thermoplastic powders. Consolidation can take place in single sided moulds using vacuum bags or in two sided moulds.

For low performance composites there are more preforming options: thermoforming continuous strand mat using two sided tools, spray application of chopped fibres using powder binders on vacuum screens followed by consolidation in two sided moulds and thermal curing, and others.

3.1.1 Thermoformed preforms using UNIFILO fibre mats

Manufacturing preforms using the thermoforming processing is one of the most commonly used methods for high volume production applications for low performance composites. The Unifilo® series of continuous strand glass mats manufactured by Owens Corning are some of the commonly used fabrics for this preforming process [29]. These fabric mats employ a thermoplastic polyester binder that is highly soluble in styrene. The forming temperature is around 180°C. The process involves clamping several layers of the fabric mat in a holding frame, the frame is then shuttled into an oven where the thermoplastic binder melts, the frame then transfers to a moulding station where a two sided tool clamps down on the hot fibres as shown in Figure 3-1. After a few seconds the mould opens and the three dimensional preform is removed from the mould. The cycle can take less than two minutes per part, shown in Figure 3-2 is a stack of preforms for a Jeep TJ hood.

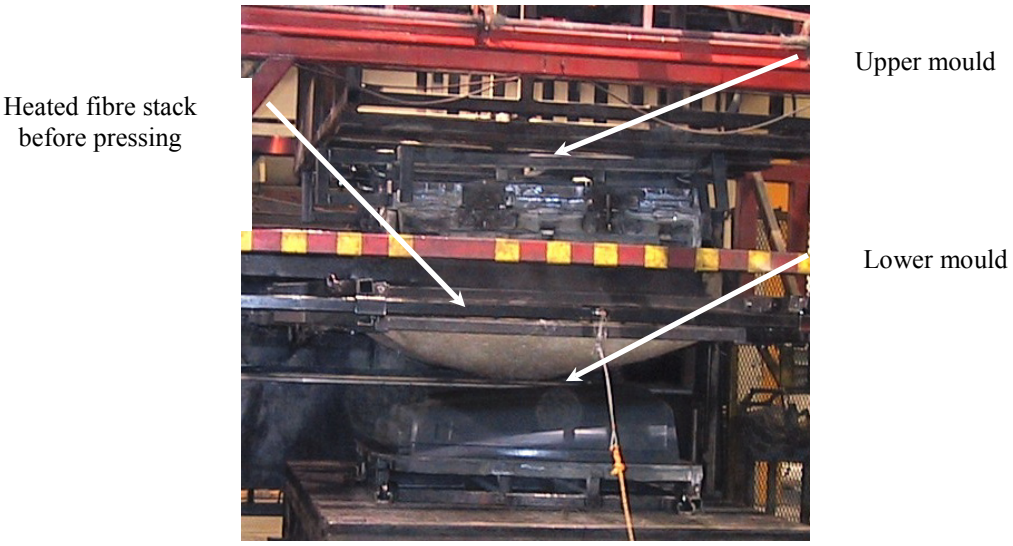


Figure 3-1 : Thermoforming method for Preforming Unifilo fabrics [30].

Figure 3-2 : Finished stack of Unifilo preforms for Jeep TJ hood [30].

There are a few limitations with this process; deep drawn parts are difficult to form due to shearing behaviour of the fabric, there is a large percentage of waste material due the rectangular transfer clamp needed to hold the sheets, and the resulting mechanical properties are low, therefore, this process is viable for low performance composite parts. This process is being used in the automotive industry, primarily for producing horizontal exterior decorative panels for low volume programs, which provide a competitive advantage over SMC moulding which requires higher cost tooling and infrastructure.

3.1.2 Preforming using Programmable Powdered Preform Process P4

The P4 process invented by a subsidiary of Owens Corning Fiberglass and the Ford Motor Company was developed to meet the needs of high volume manufacturing. This process was patented by the Ford Global Technologies, Inc. In a fully automated manufacturing cell a 12 kg preform can be manufactured in under 4 minutes [31, 32]. The main disadvantage of this process is in the consistency of the fibre density and the use of short chopped fibres. As a result the mechanical properties are low. The advantages of this process include the fast cycle times and use of low cost roving's instead of fabric mats resulting in reduced cost and waste. The principal is simple a chopper gun is used to project short chopped fibres against a heated vacuum screen. Included with the fibres is a powdered thermoplastic binder. Consolidation takes place using a second three dimensional screen. Curing is accomplished using hot air which is blown through the screen. An example of the roving delivery system is shown in Figure 3-3.

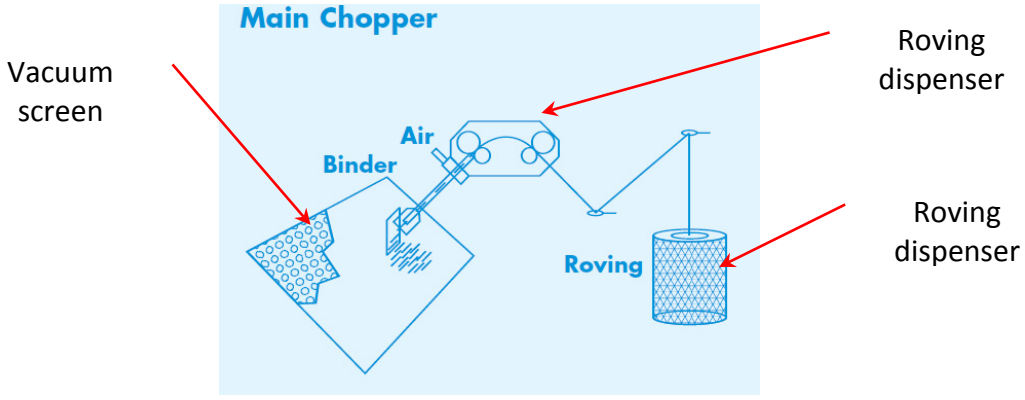


Figure 3-3 : Manufacturing principal for the P4 process [31].

Like the previously described Thermoforming process the P4 process is making inroads in the automotive industry, due to the speed and repeatability of the process; however, the resulting mechanical properties are low due to the use of chopped glass fibres.

3.2 Proposed UV cured preform process

Researchers at American GFM® started developing methods to rigidize fibre preforms in the late 1990's using directed electromagnetic energy Several patents were issued and are assigned to the C.A. Lawton Company [33]. This work started a new phase of research into fibre preforming and

the bonding of fibres to other substrates using ultraviolet light. The rapid curing capability at reduced temperatures is the primary advantage of this process.

For the PFSC process studied in this work, use of engineered fabrics is essential for creating high mechanical property parts. There is then a need for a repeatable, rapid process that can preform engineered fabric mats. Therefore, a semi automatable process is necessary to meet the goals for this mid production volume process capable of producing 45,000 units out of a single tool set or a maximum cycle time of eight minutes per part. Because the fibres in the PFSC process are placed in inner and outer thermoplastic skins, the preform process must not take more than four minutes per skin. To do this, a preforming cell has been conceived where a UV cured binder is sprayed robotically on the thermoplastic skin. Then an operator places the fibre mat directly on top of the thermoplastic skin. Finally, a vacuum bag is used to compress the fibres against the thermoplastic skin, followed by vacuum bagging. Curing is then accomplished in an automated UV chamber. The preforming and UV curing process developed in this work will be detailed in the following sections.

3.2.1 Process description

In order to develop a rapid preforming process capable of bonding the fibreglass fabric to the thermoplastic skins, curing of the fibre binder by UV light was chosen due to the speed of the curing process. UV curing is not only fast but a second advantage exists which is the reduction in heat build-up in the final part during curing. This will help to minimize the thermal mismatch between the thermoplastic skins and the fibreglass. High doses of UV radiation can be transmitted through the semi-transparent fibreglass to the UV binder on the thermoplastic skin. For the UV process, Fusion F600V UV lamps were selected. These lamps are one of the most powerful available on the market with an energy density capability of 600 W/cm^2 [34]. An Allen Bradley programmable logic controller (PLC) is used to control the lamp frame position using DC servo motors. The PLC also controls the speed the preform cart passes under the lights, as illustrated in Figure 3-4. A series of five lamps were placed in-line to span the full width of the thermoplastic skin. A picture of the actual system is shown in Figure 3-5.

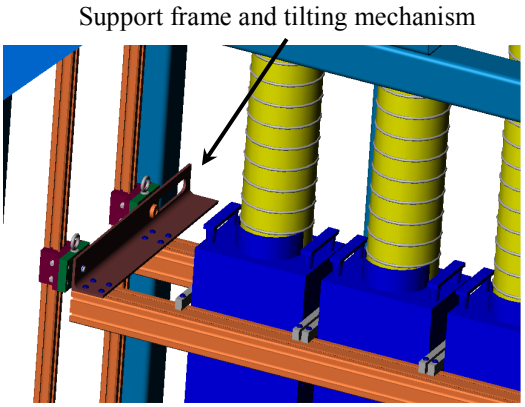


Figure 3-4: CATIA representation of the UV light support frame [35].

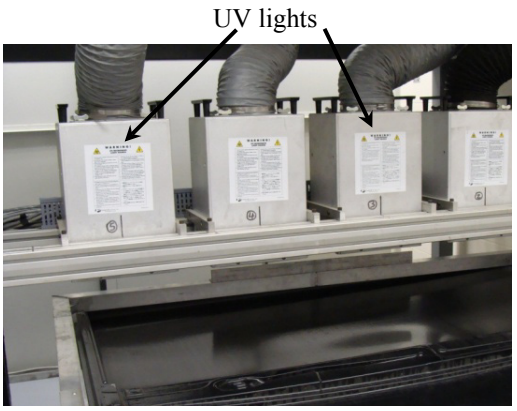


Figure 3-5: PLC controlled UV light curing system.

The support frame for the UV lights moves vertically, making it possible to control the radiation density at the surface of the part. As well, the lights can also tilt plus or minus 30° from the vertical position shown. This makes it possible to optimize the process for complex 3D parts. To protect users from high UV radiation, a booth was designed and built for this work. This system is located in the CCHP laboratory LFIC located in St-Hubert. Figure 3-6 shows a picture of the UV booth with the entry door open, the electrical control panel is on the left hand side and the preform cart is inside the booth. The preform cart is displaced automatically inside the booth using a servo-motor driven conveyor. The conveyor has a maximum speed of 20 cm/s. By combining the horizontal displacement of the conveyor and the vertical movement of the light frame, parts with relatively complex shapes can be cured with this system. Figure 3-7 depicts the capabilities of the system developed for this work, conveyor speeds (cm/sec), vertical displacement (mm) and maximum part length and width (m).

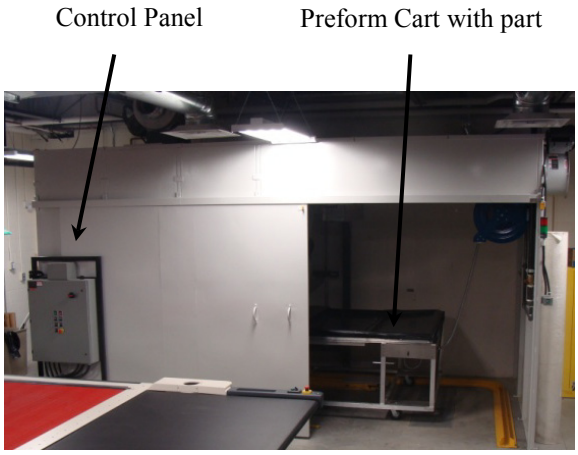


Figure 3-6: UV curing booth.

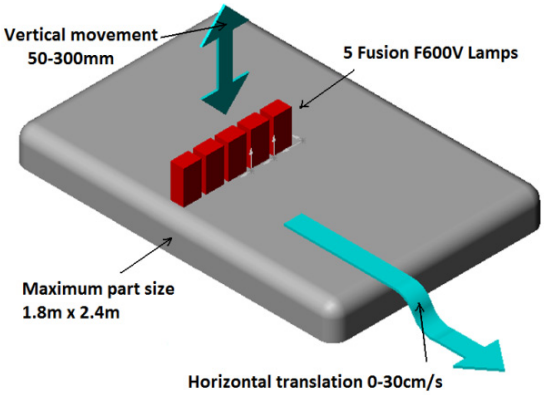
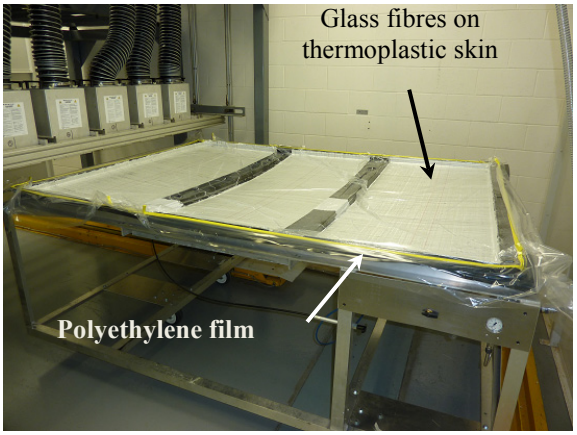
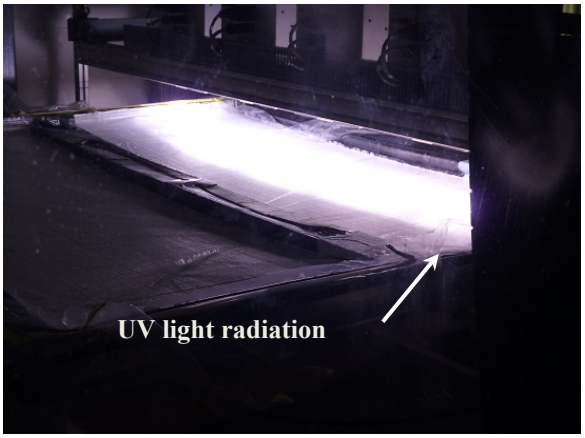


Figure 3-7: Specifications for the UV conveyor [35].

The booth and conveyor were automated using an Allen Bradley programmable logic controller. A picture of the preforming cart is shown in Figure 3-8(a). This cart serves to hold the skin in place and is also used to transport the part through the factory. The fibres are consolidated to the thermoplastic skin by using a vacuum clamping system. Air is evacuated between the thermoplastic skin and fibre mat under a thin film of polyethylene deposited on the surface of the fibres. Curing is shown in Figure 3-8(b).



(a)



(b)

Figure 3-8: UV preforming showing: (a) cart with preform and (b) the curing process.

3.2.2 UV process development

3.2.2.1 Characterization of the UV curing unit

The preliminary step after constructing the UV booth and conveyor was to determine the curing characteristics of the UV chamber. With this information the binder optimization and resin formulating may follow. This characterization was done in partnership with the Centre de développement des composites du Québec (CDCQ) and the Centre technologique en aérospatiale (CTA) [36], both interested in using the system developed in this study.

The spectral range for ultraviolet radiation is between 240 and 750 nm shown in Figure 3-9. The UV domain is divided into four main categories of radiation: UVA (320 to 390 nm), UVB (280 to 320 nm), UVC (240 to 280 nm) and UVV (390 to 445 nm). In order to understand the behaviour of the radiation lamps, the energy density emitted was analyzed using a UV radiometer.

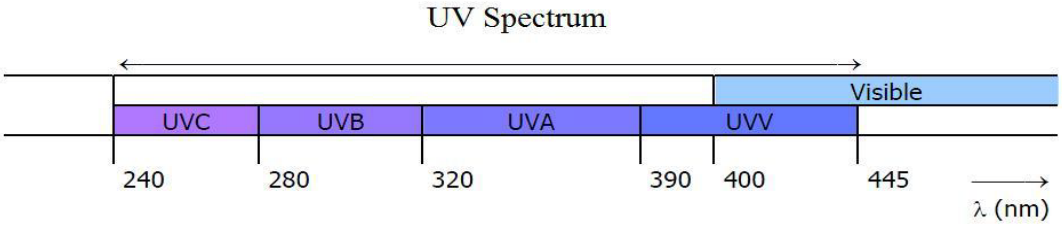


Figure 3-9: Spectral range for ultraviolet radiation.

The UV lamps selected for the chamber were microwave brand Fusion UV (model F600) equipped with a bulb type V (Mercury-Gallium). These lamps emit predominantly UVV radiation. The UVV spectrum is advantageous when curing adhesives where deep light penetration is necessary.

Two key parameters were measured during this characterization. The power density or UV intensity which is a measure of the energy flux averaged over a period of the wave. It is synonymous of the strength or amplitude of the radiation. The UV intensity is measured in units of mW/cm^2. The second parameter is the UV dosage which is the product of UV intensity (expressed as energy per unit surface area) and residence time. Therefore: $DOSAGE = I \times T =$ mJ/cm^2.

The characterization of the chamber was completed using a UV radiometer which measures UV dosage (mJ/cm^2) and thermal flux or UV intensity (mW/cm^2). The results obtained were analyzed

using the PowerView software supplied with the instrument. The process of characterizing the UV system involves understanding the radiation across the entire surface of the part. A series of experiments were completed looking at the vertical distance of the lamps from the part, the distance between the lamps and the speed the part passed under the lamps. Analysis of this information will aid in optimizing the parameters for the UV curing process and in the selection of the best UV binder.

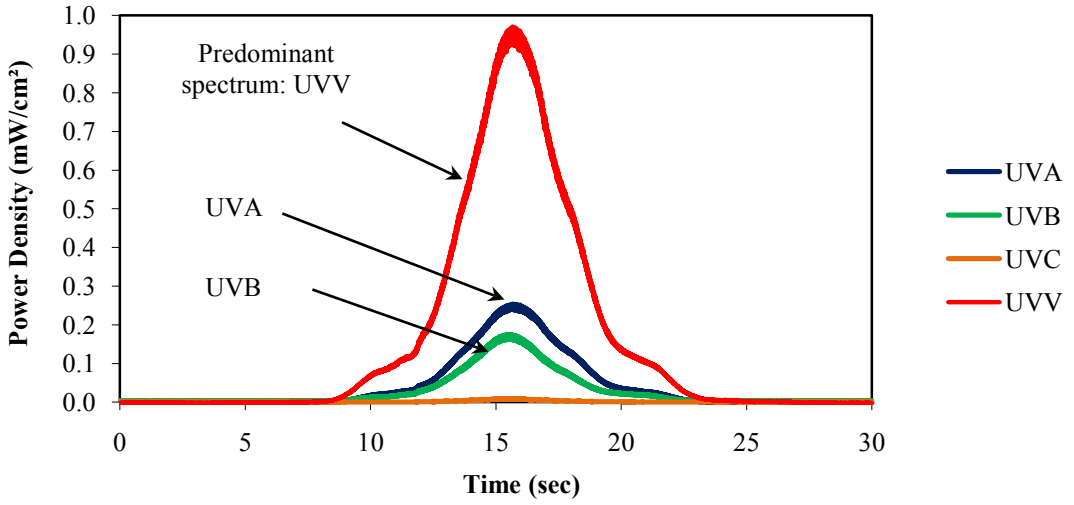


Figure 3-10: Measurement of the spectral range at distance of 30 cm from the part.

The Power Density for the four categories of UV radiation (ABCV), emitted at a distance of 30 cm from the part are shown in Figure 3-10. As expected the UVV energy density is predominant, because of the selection of Mercury-Gallium bulbs; however, there are measureable quantities of UV A, B and C emitted as well. By understanding the power density capabilities of the system as well as the curing requirements for the UV binders, it is possible to optimize the curing parameters of the system, i.e. conveyor speed, distance from the lamp the part and spacing distance between the lamps.

To evaluate the different variables that influence the radiation dynamics, an initial plan of experiments was developed. For this series of tests the radiometer was positioned on the axis transverse to the lamps at (46, 61, 72, 79, 81, 91, 107 and 122 cm from the reference left). The speed of the cart was held constant at 45 mm/second and the distance between the lamp and the radiometer were constant at 30 cm.

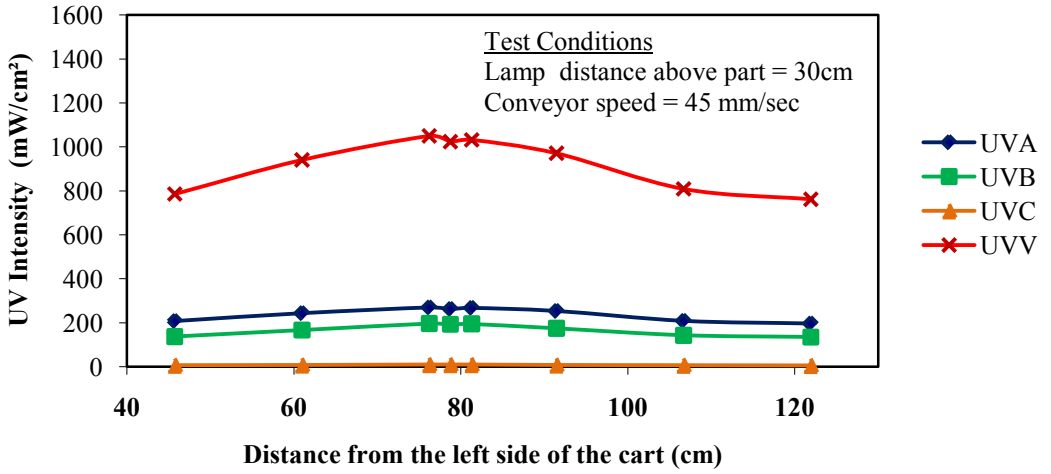


Figure 3-11 : UV light intensity across the width of the cart.

The data was analyzed to determine the intensity emitted by the UV chamber. Knowing the sweep speed used during a test, the basic equation the kinematics (velocity = distance / time) can also represent the curve obtained according to the position of the lamp. Data from various screening trials has shown that the UV intensity is not constant over the entire width of the part, as illustrated in Figure 3-11. This information can be used to either reposition the distance between the lights, to minimize variations created by light overlapping. Or to change the distance from the lamp from the part, to again minimize the overlapping effect, (see Figure 3-12). If the minimum UV intensity exceeds the curing requirements for the UV binder light adjustment may not be required.

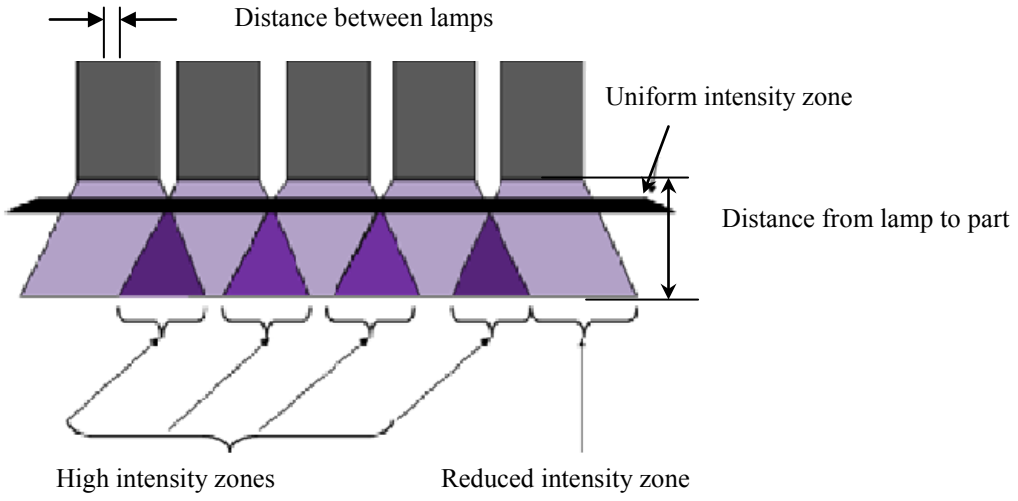


Figure 3-12 : Radiation effects due to light overlapping.

The next set of experiments involved changing the conveyor speed from 45 to 75 mm/s. As described earlier this will not affect the UV intensity; however, the UV dosage will be affected as shown in Figure 3-13. The UVV dosage is again dominant compared to the UV B and C. The UV dosage reduces as a power function as shown on the graph.

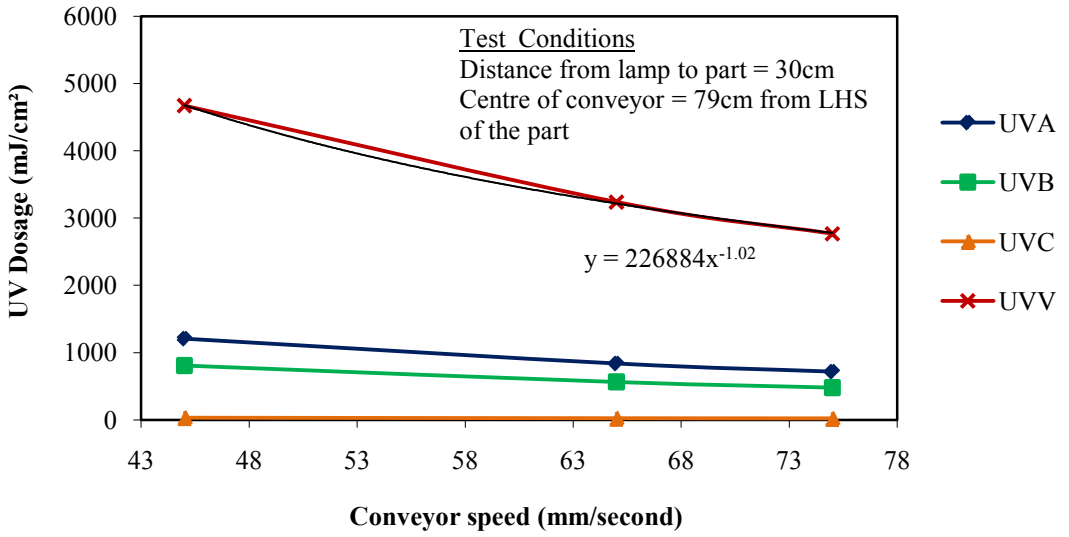


Figure 3-13 : UV Dosage along the length of the part for different conveyor speeds.

The last critical set of experiments involved measuring the decay of the radiation due to absorption effects of the fibreglass mats. In order to insure sufficient curing of the UV binder under the fibreglass preform, a series of tests were carried our measuring the UV dosage as a function of the number of fibre layers. As can be seen in Figure 3-14, after adding one layer of bi-directional glass fabric the UV dosage dropped 73%. Adding a second layer of glass fabric, the dosage dropped another 68%. This significant drop in available curing energy was one of the reasons for selecting the Fusion 600 lamp system which is one of the most powerful lamp systems available on the market. Because the available UV energy is low, even with these high power units, it is important to develop UV resins with extremely efficient photo initiators.

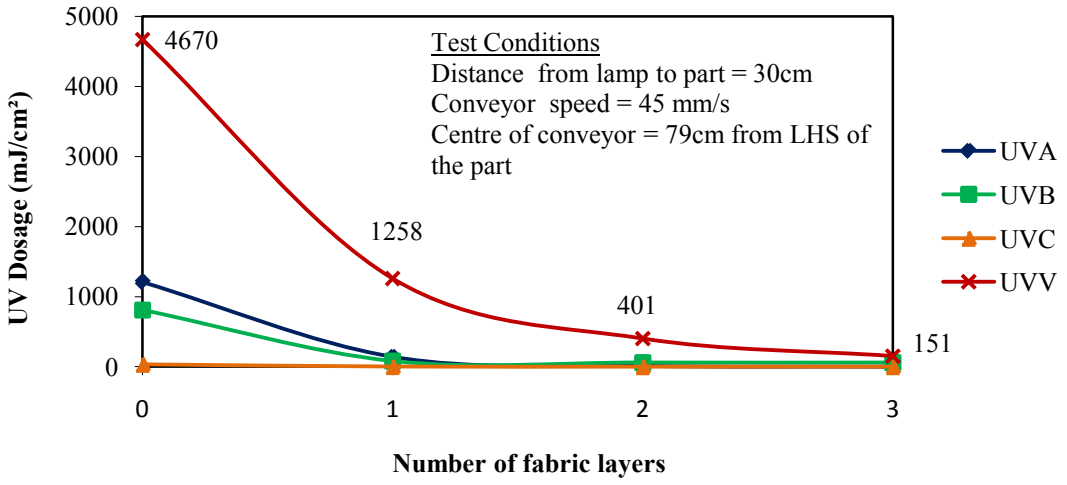


Figure 3-14 : UV dosage measured through several layers of glass fabric.

3.2.2.2 Properties of UV binders

The UV cured binder plays a key role for the manufacturing process developed in this work. At the beginning of this project there was a small sample of UV curable resin (Permabond LL-491) was available for testing. This material was the first generation of UV curable resin used in the PFSC process. The technical data sheet for this resin can be found in Appendix B. Since this material is no longer commercially available, a replacement resin was required. A partnership was created with a local company "Inortech Chimie", located in Terrebonne QC. Roger Mouhana the UV specialist produced more than 10 prototype UV adhesives used in this work, eventually reducing to a single product now commercialized as CB 601.

The requirements of the binder are as follows: the UV binder must bond well to both the thermoplastic substrate and to the E-glass fibres. Also, there should be good compatibility with the PUR foam to prevent any negative interactions such as gassing or delamination. After a material research and screening study the Urethane Acrylate family of resins were selected. To achieve a high degree of cure under the fibreglass mat the photo initiator has to be activated in the UVV spectrum, according to the results of Figures 3-11 to 3-13. This spectrum makes it possible to cure the binder with up to two or three layers of fibreglass (see Figure 3-14).

Another desirable characteristic for the UV binder for this preforming application is aid in anchoring the fibres to the thermoplastic it must have a high viscosity, (up to 20,000 cps). The resin will be sprayed on the thermoplastic skin as shown in Figure 2-17, in a droplet pattern. The

droplets act as hooks when contacting the fibreglass, acting like small stitches which hold the fibre next to the thermoplastic. Also, by reducing the surface coverage of the binder on the thermoplastic skins the PUR foam will act as the primary bonding system for the thermoplastic skin. The UV binder will therefore carry a reduced load making it possible to have lower mechanical properties than the PUR foam. Also, the cost of the UV binder (around $50/kg) is much higher than the PUR foam (at $2/kg), therefore minimizing the binder is desirable.

3.2.2.3 Screening test results

In the screening test protocol three different UV curable binders were investigated: Permabond LL-491, Loctite® 3106™ and Inortech's CB600. The properties of these binders are summarized in Table 3-1.

Table 3-1 : Comparison of the UV binders used in the screening study.

Material	Manufacturer	Chemical Composition	Viscosity (cP) at 25°C	Minimum Intensity (mW/cm^2)	Specific Gravity (g/cc)	Cost (S/kg)
Loctite 3106	Loctite®	Acrylate urethane	7500	50	1.08	300
LL-491	Permabond	Acrylate mixture	20,000	unknown	1.07	Na
CB-601	Inortech Chimie	Urethane Acrylate and Oligomer Acrylate	14,000	172	1.05	50

A series of samples were prepared by UV curing strips of fibreglass to L shaped thermoplastic samples as shown in Figure 3-15. The T-peel resistance tests were carried out was the according the ASTM D1876-08 standard. These tests were conducted using the MTS machine. The crosshead speed of the MTS was set at 4 mm/sec, and the peel resistance was recorded in Newton's. The results are listed in Table 3-2.

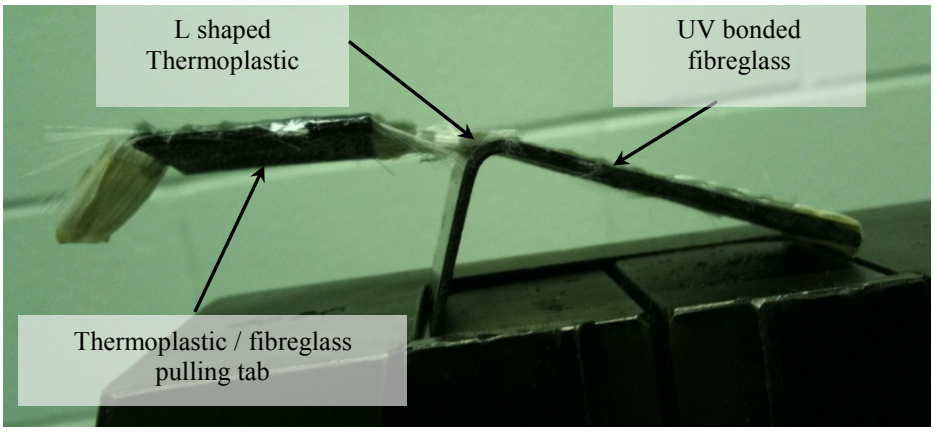


Figure 3-15 : Peel test specimen with glass fabric and PC/ABS thermoplastic.

The samples were fabricated using strips of thermoplastic, covered with a larger sheet of glass fabric. The adhesive was applied using a paint brush and then consolidated using a vacuum bag as shown Figure 3-16. After UV curing the samples were separated. This identical procedure was applied to the three different UV binders. A total of fifteen replicates were made for each material.

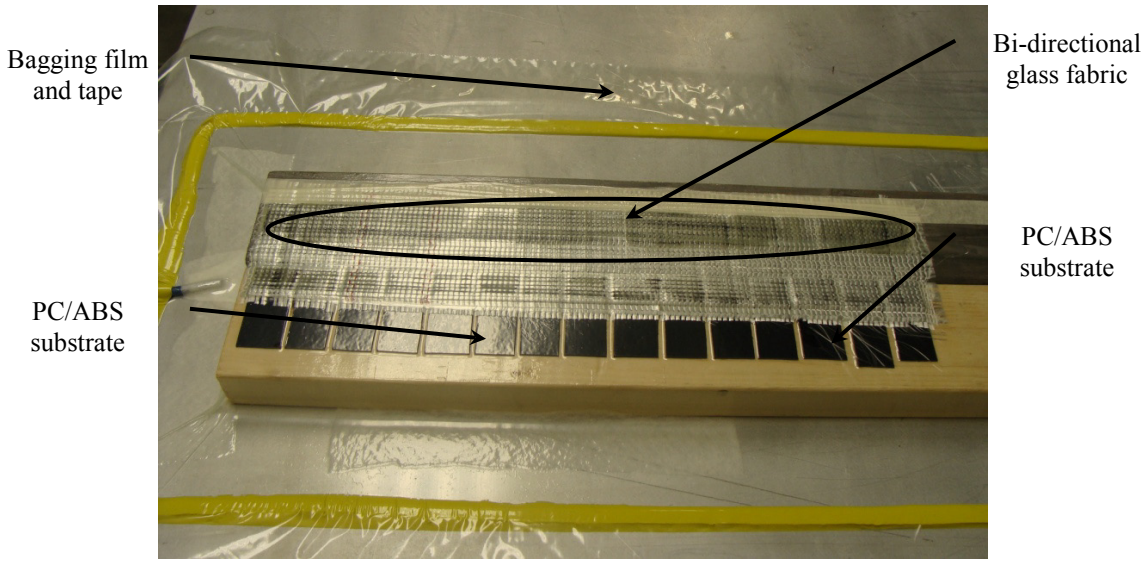


Figure 3-16 : Preparing specimens for the peel test.

Table 3-2 : Results of the peel tests for the three UV cured adhesives.

Company	Name of the UV-adhesive	Relative peel strength [N] x [mm] of debonding				
		10 mm	20 mm	30 mm	40 mm	50 mm
Permabond	LL- 491	24	9	5	3	0
Loctite	3106	69	60	53	26	4
Inortech	CB-601	21	66	49	36	19

The relative peel resistance of the first series of tested adhesives show two different behaviours: with the Permabond adhesive, the relative peel resistance drops quickly to zero. The Loctite 3016 adhesive has the highest peel strength but the adhesion drops abruptly after 32 mm of travel is reached. The Inortech CB-601 has a lower peak peel strength than the Loctite adhesive but continues to hold on to the substrate even after 50 mm of debonding, (see Figure 3-17).

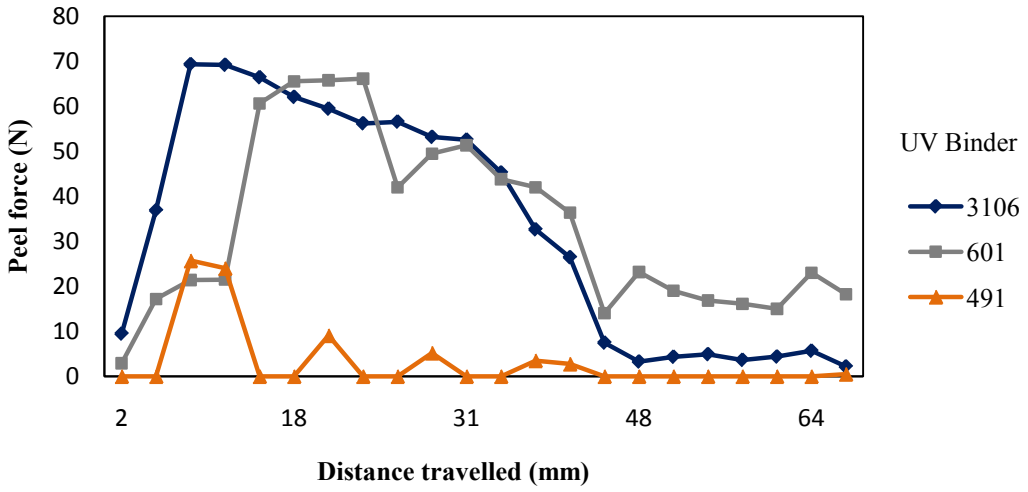


Figure 3-17 : Results for the T-Peel tests performed on PC/ABS with fibreglass.

The glass transition temperature was measured on binder samples and the thermoplastic according to the ASTM D-3418 standard. The results are listed in Table 3-3. For comparison purposes, the *Tg* for the PUR foam is also listed. The results show that the foam and the

thermoplastic skins both have a much higher *Tg* than the binders. The Permabond material has the lowest *Tg* and its low strength was confirmed in the previous peel tests.

Table 3-3 : Glass transition temperatures results for UV binders and PC/ABS

Company	Name of the material	*Tg* [°C]	Comment
Permabond	LL- 491	17	The transition temperature is below room temperature.
Loctite	3106	55	
Inortech	CB-601	50	
PC/ABS (sheet material)		113	From literature *Tg* of PC/ABS blend 125°C [37]
PUR Foam (see Table 5-7)		115	Based on formulation with Isocyanate index 140

The Tensile modulus was measured across a wide range of temperatures using a Dynamic Mechanical Analyzer (DMA) instrument. The target maximum use temperature for the sandwich composite developed in this work is around 80°C. Therefore, it is important to study the behaviour of the adhesive through this temperature range. If the mechanical properties of the adhesive are too low, delamination or the creation of blisters can occur.

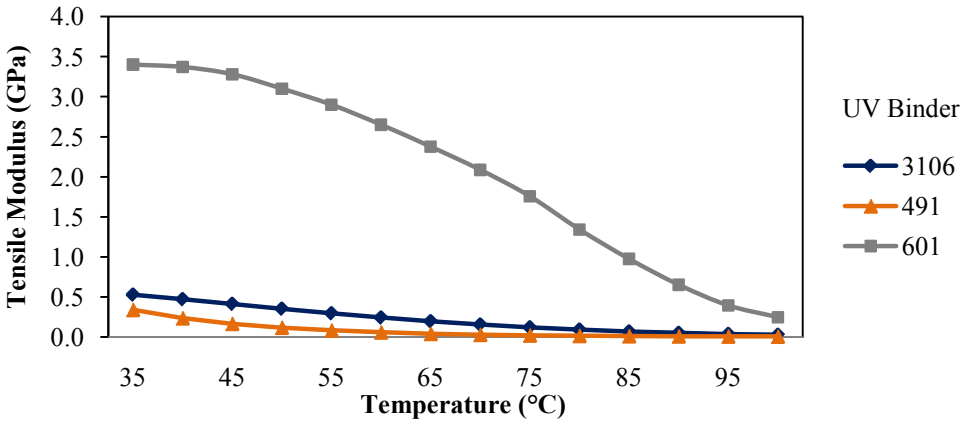


Figure 3-18 : Tensile modulus versus temperature for the UV cured binders.

Figure 3-18 shows the moduli variation as a function of temperature for the different adhesives. The CB601 binder had the highest starting modulus (3.4 GPa) at room temperature, dropping to 1.34 GPa at 80°C. The LL-491 has the lowest initial modulus at less than 300 MPa at room temperature and 0 MPa at 80°C. The increased modulus of the CB-601 should impart higher temperature resistance in the final composite part. As well, the higher peel strength will reduce the tendency for the foam to shear the fibres off the thermoplastic skin during resin injection, therefore reducing moulding defects.

3.2.3 Summary and conclusions for the UV process development

The new UV curing system was fully characterized in this work. The automation equipment designed and built facilitated the rapid change of process parameters such as distance from the part surface and conveyor speed. The optimized settings for the conveyor are as follows: distance from lights to part (30 cm), conveyor speed (45 mm/min). Using these parameters and curing a sample with a single fibreglass fabric layer, the UV binder will receive a dosage of more than 1000 mJ/cm^2. This dosage level will ensure deep curing of the UV binder.

Three different UV binders were characterized. With the assistance of Inortech Chimie, a new material was developed and recently commercialized. The trade name for this new binder is CB-601. Characterization of these materials involved conducting T-peel tests, dynamic mechanical thermal analysis using the DMA instrument and glass transition measurements (*Tg*) using the differential scanning calorimeter (DSC) instrument. The CB601 exhibited improved debonding

energy compared to the other binders, as well, elevated modulus through the temperature range and finally a mid range glass transition temperature (*Tg*) equal to 50°C.

CHAPTER 4 POLYURETHANE FOAM DEVELOPMENT

4.1 Introduction to polyurethane foam fundamentals

Polyurethane foams are produced for a wide range of applications thanks to their tailored properties from elastic, visco-elastic to rigid foams. Another advantage of polyurethane processing is the ability to mould complex three dimensional shapes with engineered properties.

In this project polyurethane is used to fabricate complex sandwich structure composites. The polyurethane chemistry developed for this application is in the rigid foam family employing a polymeric isocyanate (pMDI) and a blend of polyether polyols. This polyurethane foam is in the isocyanurate family where the stoichiometric proportions are not balanced. Through the use of a trimerization catalyst, excess isocyanate used in the formulation reacts with itself to produce additional hard segment domains. The result is polyisocyanurate foam with increased modulus and increased glass transition temperature (Tg).

The polyisocyanurate foam is blown using an auxiliary blowing agent based on the hydro-fluorocarbon family (HFC) and water. The blowing agent selected is non ozone depleting and low greenhouse gas emitting [38]. This blowing agent reduces the viscosity of the polyurethane foam during injection; as well it delays the reaction by absorbing heat from the reacting foam. These two effects facilitate the wetting of the reinforcing glass fibres in the part.

4.1.1 Polyurethane Foam Basics:

Polyurethanes are formed from multiple ingredients and at least two simultaneous reactions. The urethane reaction occurs when the Isocyanate and Polyol are combined as shown in equation (4-1).

$$\underset{Isocyanate}{R-N=C=O} + \underset{Polyol\ Alcohol}{R'-CH2-OH} \xrightarrow{-\Delta} R-\underset{\underset{H}{|}}{N}-\underset{\underset{Urethane}{\|}}{\overset{O}{C}}-O-CH2-R' \qquad (4\text{-}1)$$

To make foam the polyurethane, the polymer is blown by the formation of carbon dioxide in situ and or through the use of auxiliary non reactive chemicals that absorb vaporize during reaction providing additional gas which blows the liquid polymer.

For the polyurethane mixture under investigation, water is used at low concentrations, minimizing the creation of CO_2. A hydrofluorocarbon (HFC) is used as the primary blowing agent. Hydrofluorocarbons are organic compounds with one or a few fluorine molecules [39]. A secondary benefit of the hydrofluorocarbon blowing agent is the creation of a thick, high density skin on the surface of the polyurethane foam. This skin is created when the internal pressure of gas inside the foam bubble exceeds the tear strength of the developing polyurethane. At the surface of the mould energy is drawn from the reacting foam thereby slowing down the development of molecular weight locally. Under these conditions the foam cells collapse at the surface and cause the foam density to increase locally.

$$\underset{Isocyanate}{R-N=C=O} + \underset{Water}{H-O-H} \xrightarrow{-\Delta} \underset{Amine}{R-N-H2} + \underset{Carbon\ Dioxide}{CO2\uparrow} \tag{4-2}$$

$$\underset{Isocyanate}{R-N=C=O} + \underset{Amine}{R'-N-H_2} \xrightarrow{-\Delta} R- \underset{H}{N-} \underset{}{\overset{\overset{O}{\|}}{C-}} \underset{H}{N-R'} \tag{4-3}$$

$$Undistributed\ Urea$$

There are three consecutive reactions that take place during the formation of polyurethane. First the water reacts with the isocyanate to create CO_2 gas which diffuses into the cells of the foam where dissolved nitrogen and dissolved oxygen are present in the liquid. This initiates the blowing of the foam. At the same time an unstable carbamic acid is formed which decomposes and forms an Amine. The amine continues to react with the available isocyanate forming undistributed urea as shown in equation (4-3). This occurs when the isocyanate reacts with the developing amine molecules or with the added amines in the mixture. The urea formed is not very soluble in the reacting mixture forming hard segments in the polyurethane foam.

4.2 Polyurethane resin components and their properties

The polyurethane foam is made by blending several ingredients to form the resin, followed by mixing the blended resin with an isocyanate.

A typical polyurethane resin is comprised of a polyol (polyether or polyester) which makes up approximately 80 % of the resin. A common resin formulation is presented in Table 4-1. In order to promote cell regulation and cell stabilization a silicone surfactant is added at proportions of up to two parts per hundred parts of resin (phr). To promote the blowing and gelling of the polyurethane foam an amine catalyst is often used. In the case of isocyanurate foams a secondary amine catalyst up to 2 phr is used to change the rates of reaction in order to make additional heat available to the isocyanate in order to allow the isocyanate to form distributed urea. Low amounts of water, around 1 phr are used to produce carbon dioxide and promote stability. Higher levels of water accelerate the reaction which in turn can impede the formation of the surface skin which is necessary for the sandwich composite. Lastly, the hydrofluorocarbon blowing agent is added at levels up to 15 phr. At atmospheric pressure the hydrofluorocarbon will start to vaporize at 20.5°C (69°F). It is therefore necessary to keep the mixture under pressure to minimize vaporization. The equations to determine the final mass ratio for the polyol mixture and the isocyanate, based on stoichiometric proportions are shown below with example calculations.

The most common way to evaluate rigid foams is to modify the stoichiometric proportions of the reactive components. The stoichiometric proportion is evaluated through the isocyanate Index, which is defined as the ratio of isocyanate functional groups and available hydroxyl groups (NCO/OH) see equation (4-4).

$$Isocyanate\ Index = \frac{Actual\ amount\ of\ Isocyanate\ used}{Theoretical\ amount\ of\ isocyanate\ required} x100 \qquad (4\text{-}4)$$

Additionally the isocyanate index can be calculated using the equations in Table 4-1. These equations are useful in determining the stoichiometric proportions of the components. The isocyanate index and ratio of the A and B components can be calculated as follows [40]:

Table 4-1 : Polyurethane resin formulation

Resin B side	**Chemical Name**	**% by total Weight**	**HEW (Hydroxyl equivalent weight)**	**Specific Gravity (g/cc)**	**# of Equivalents. (HEW x %Weight)**
Polyol	Voranol 335	82	168	1.0685	0.4881
Water (H_2O)		0.70	9	1	0.0778
Surfactant	DC-197	2.50		1.06	
Primary Catalyst	Polycat 77	1.25		0.851	
Secondary Catalyst	Curithane 52	2.42	106	1.1	0.0228
Blowing agent	HFC245FA	11.13		1.25	
Total		100		1.092	0.5888

Isocyanate A side	**Chemical Name**	**Parts**	**IEW (Isocyanate equivalent weight)**	**Specific Gravity (g/cc)**	**# of Equivalents. (IEW x %Weight)**
pMDI	PAPI 27	126.5	134.3	1.2	0.9419
Index (NCO/OH)		160 (desired)			
A/B ratio		1.265			

Calculations for the proportions of the polyol mixture and isocyanate from the formulation in Table 4-1 needed to achieve an isocyanate index of 160.

A-Side: The Isocyanate containing material (NCO)

$$Equivalent\ weight\ of\ the\ isocyanate = \frac{4200}{NCO}\ \text{g/eq} \tag{4-5}$$

In equation (4-5), 4200 represents the molecular weight of NCO in mg/mol

Example: NCO content for polymeric MDI (pMDI) = 31.27 % [41] (4-6)

$$Equivalent\ weight\ pMDI = \frac{42X100}{31.27} = 134.3\ g/eq$$

$$Equivalents\ iso = Equivalent\ weight\ x\ parts = 134.3\ x\ 126.5 = 0.9419 \tag{4-7}$$

The parts shown in equation (4-7) are referenced in Table 4-1.

B-Side: The blended Polyol (OH)

In order to calculate the mass of polyol in stoichiometric proportions you need to calculate the equivalent weight of the polyol mixture based on the hydroxyl number (OH number) of each component. The OH number is expressed in mg KOH/g, which represents the relative amount of hydroxyl groups per gram of each component.

$$Equivalent\ weight\ of\ polyol\ = \frac{56{,}100 +}{OH\ Number} \tag{4-8}$$

In equation (4-8) +56,100 represents the molecular weight of KOH in mg/mol. Equivalents of the polyol mixture represent the reactive sites of OH available to react with the reactive sites of isocyanate (NCO)

$$Equivalent\ weight\ of\ polyol = \frac{Mass\ of\ Polyol}{Equivalent\ Weight} \tag{4-9}$$

$$Equivalent\ weight\ of\ polyol\ = \frac{100}{\frac{Wt\%\ Polyol\ A}{Eq.Wt.Polyol\ A} + \frac{Wt\%\ Polyol\ B}{Eq.Wt.Polyol\ B} + \cdots}$$

From Table 4-1 the values for HEW for each component are listed.

$$Equivalent\ weight\ of\ polyol = 100/\left(\frac{82}{168} + \frac{0.7}{9} + \frac{2.42}{106}\right) = 169.86 \quad (4\text{-}10)$$

$$Equivalents\ polyol = Equivalent\ weight\ x\ parts = 169.86\ x\ 100 = 0.9419 \quad (4\text{-}11)$$

To calculate the ratio B/A based on equivalent for a desired index of 160:

$$160 = \frac{B}{A} = \frac{(Equivalents\ B - Side)}{(Equivalents\ A - Side)} = \frac{0.9419}{0.5888} x100(stoichiomentric) \quad (4\text{-}12)$$
$$= \frac{126.5}{100}(actual)$$

Therefore based on the formulation in Table 4-1, and using the above calculations, to achieve an index of 160 using stoichiometric proportions the ratio of isocyanate to polyol is 1.265.

4.3 Characterization of the free rise foam behaviour

In order to characterize the polyurethane reaction it is important to measure the thermal and kinetic events. Figure 4-1 illustrates the physical, kinetic and morphological events which take place during the formation of polyurethane; diffusion, blowing, gelling, gas blow off, etc. [40]. These events are difficult to monitor inside the mould therefore in the practice of optimizing foam formulations it is common to evaluate the foam behaviour in free rising atmospheric conditions. The start of polymerization is determined by carefully observing the foam after injection into the open container. The start of polymerization (cream time) can be seen when the reacting mixture appears to curdle soon after injection. The point of gelation is measured using a small wood or plastic stick. The stick is manually inserted into the developing foam and removed slowly. The point where a thread appears between the residue on the stick and in the liquid the gel point is identified (string gel). Lastly when the foam reaches full height there is another change in state of the foam. The surface goes from a sticky solid to a non sticky solid (tack free).

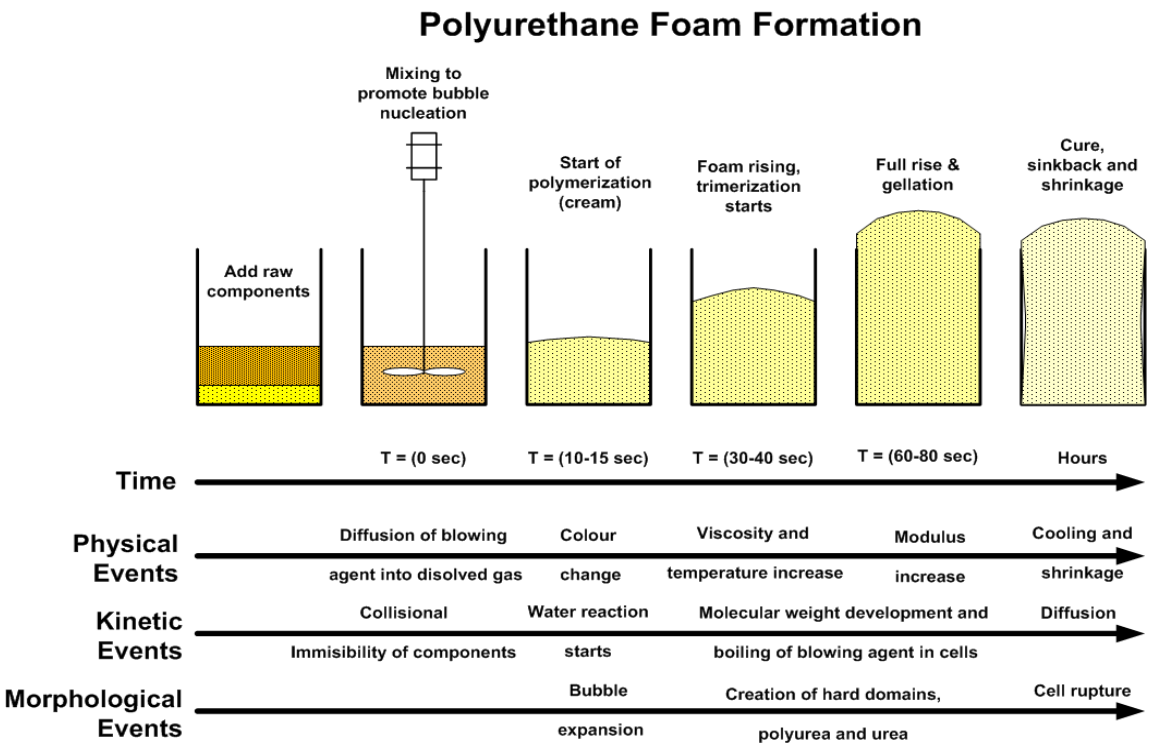


Figure 4-1: Sequence of events during polyurethane foam formation [40].

The two component foam recipe, (polyol mixture and isocyanate) is dispensed using a two component high pressure foam injection system (Cannon A200). To prepare for this work the injection system was completely overhauled and a high pressure manifold was designed and installed which made it possible to operate three independent mix-heads with one injection system (see Figure 4-17). The injection system is shown in Figure 4-2.

Figure 4-2: Cannon A200 polyurethane injection machine.

The two components are mixed using a high pressure impingement mix-head (Cannon FPL24 mix-head). The mix-head is shown in Figure 4-3.

Figure 4-3: Cannon FPL 24 Mix-head mounted in mould.

For the experiments using the characterization stand and mould, the resin was injected at a constant flow rate of 1000 g/s, while the impingement pressures were set at 7000 kPa (70 bars) for each component. The ratio of the polymeric methylene diphenyl diisocyanate (pMDI) and polyol resin blend was varied to achieve the desired stoichiometric proportions. The method used to calculate the stoichiometric proportions will be described in section 4.2.

To aid in the development of the resin system used in this work, a test bench was developed to measure the critical events. The characterization tools developed in this study are shown in Figure 4-4. This fixture employs a digital scale to measure the gas losses that occur during the chemical reaction. A sonar probe is used to measure the rise profile of the foam and six thermocouples are used to capture the exothermic behaviour. In parallel, a second test is conducted where three key parameters are observed: cream time (start of polymerization), string gel (practical gel point where foam becomes a solid), and tack free point (surface of foam appears cured and is not tacky to the touch). A data acquisition system was developed using Texas Instruments Labview software and three hardware modules. Figure 4-5 shows the user interface for the data acquisition software used with this characterization fixture. The temperature, rising profile of the foam, and mass loss are recorded in time and shown on the screen.

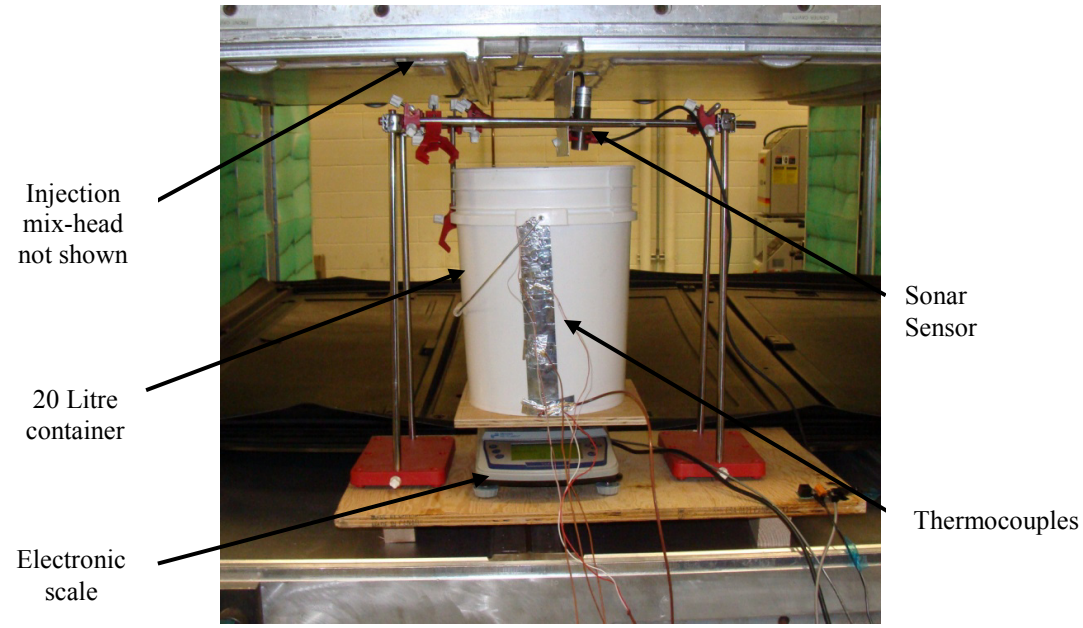


Figure 4-4: Foam free rise test fixture developed in this work.

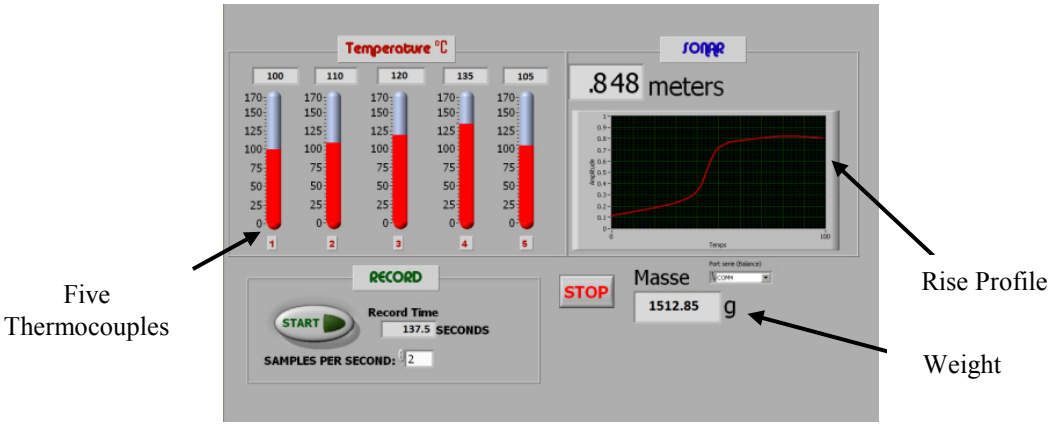


Figure 4-5 : Computer software interface developed in this work.

This characterizing equipment makes it possible to optimize some of the key processing conditions for the foaming system before moving to injections in a closed mould. A typical plot from the free rise apparatus is shown in Figure 4-6.

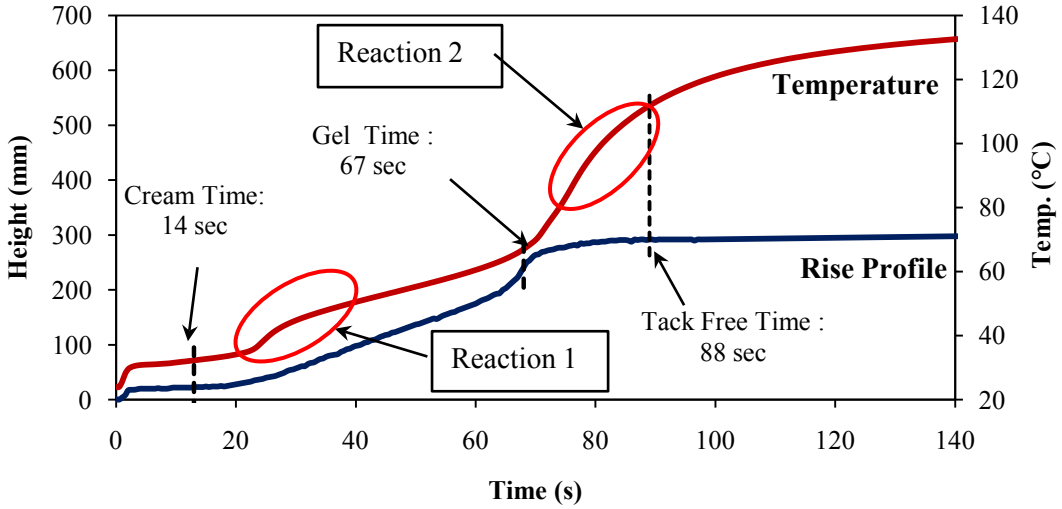


Figure 4-6: Results using characterizing tools for free rising foam.

Comparing the free rise behaviour from the plots and examining the morphology of the foam can identify areas of instability in the reaction kinetics. Cross sections cut through the cured foam samples will identify mixing issues, cell structure regularity and instability of the foam as represented by splits in the foam. Some of these conditions are shown in Figures 4-7 and 4-8.

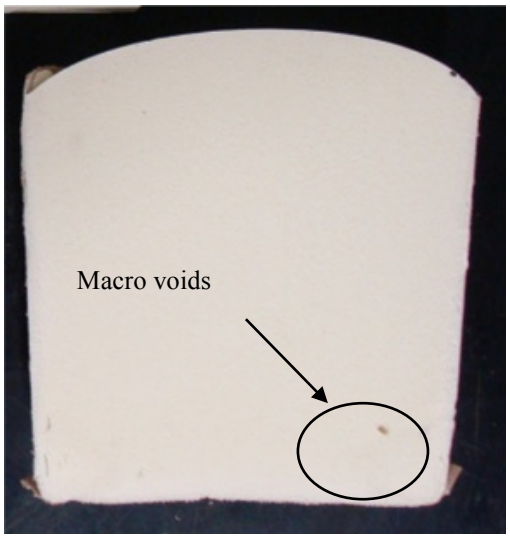


Figure 4-7: Cross section of foam.

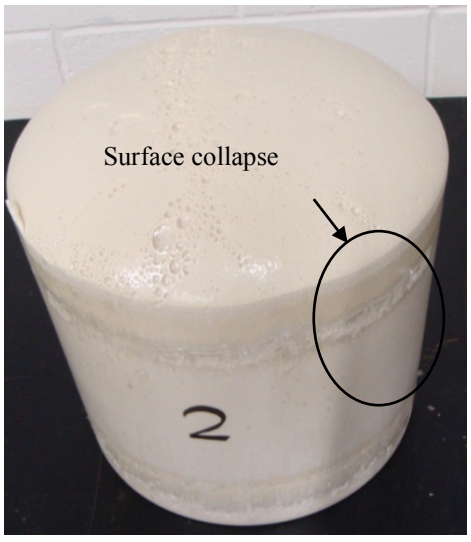


Figure 4-8: Foam bun with collapse.

4.4 Characterizing the foam under pressure moulding conditions

The characterization equipment developed in section 4.3 offers some insights into the behaviour of the foam; however, there are significant differences when foaming under pressure. Characterizing the foam under a pressure environment similar to real moulding conditions is one of the primary goals of this work. The novelty of this process is in the ability to wet out dry fibreglass with the reacting polyurethane foam while at the same time create a low density foam core; therefore it is essential to understand the conditions which facilitate this complex behaviour.

In this work a second set of characterization tools was developed to understand this behaviour. The principal was simple, use a 9 L pressure pot to simulate a mould, develop a new lid which makes it possible to inject the foam directly into the container with instrumentation to measure the impedance of the foam, the real time pressure in the mould and the exothermic behaviour. In addition to the instrumentation a sight window was incorporated in the mould to make it possible to see the saturation of the fibres in real time.

Photographs of the various characterization equipment and ancillary components developed in this work are show in Figure 4-9. The polyurethane resin is injected directly into the closed mould using a 25 mm diameter hose. A new venting system was developed to create a liquid barrier between the vacuum system and the mould; this will be described in more detail later. Full vacuum is applied to the cavity using a Reitchle VC 500-20 Hp vacuum pump capable of reaching 0.1 mbar (abs.). The vacuum pump is not shown; however, a vacuum reservoir is shown which is used to protect the vacuum system in the event resin gets past the vent.

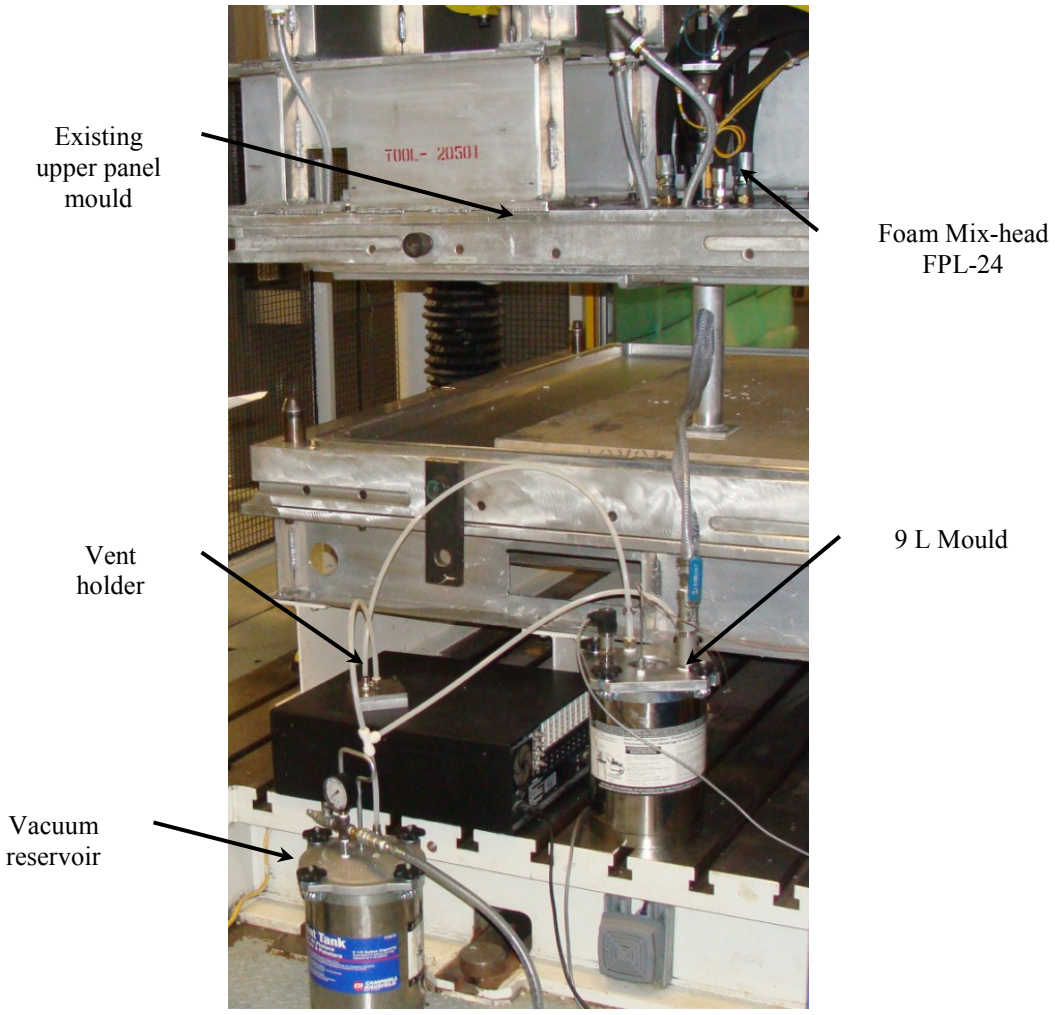


Figure 4-9: System for characterizing the foam under pressure conditions.

Pictures of the vent holder are shown in Figure 4-10. The material used for the holder is steel. The liquid enters the vent along the perimeter of the chamber as indicated. Vacuum is applied to the centre of the block as shown by vacuum outlet. The disposable vent is made from a porous ultra high molecular weight polyethylene (UHMW). The nominal particle diameter is approximately 500 µm. When the liquid polyurethane enters the vent it flows around the perimeter while slowly saturating the vent. When gelation occurs the foam stops flowing creating a barrier between the vacuum system and the mould.

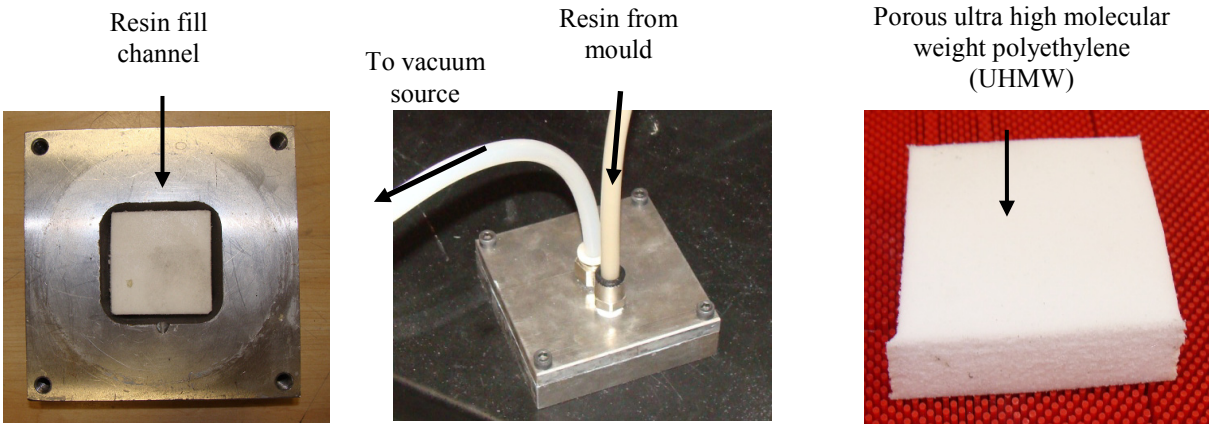


Figure 4-10 : Vent holder assembly.

In order to inject the resin directly into the new mould a series of components were conceived. The challenge was to inject the foam from a mix-head that is mounted in an existing mould without removal. This was accomplished using a custom guide holder and hose adapter. The guide holder was held securely in the existing mould under pressure from the hydraulic press not shown. A pressure of 50 T was applied to the holder to prevent vacuum and foam resin from leaking. The assembly and holder are shown in Figure 4-11. This device reduced setup time between experiments with the new mould and the press mounted mould.

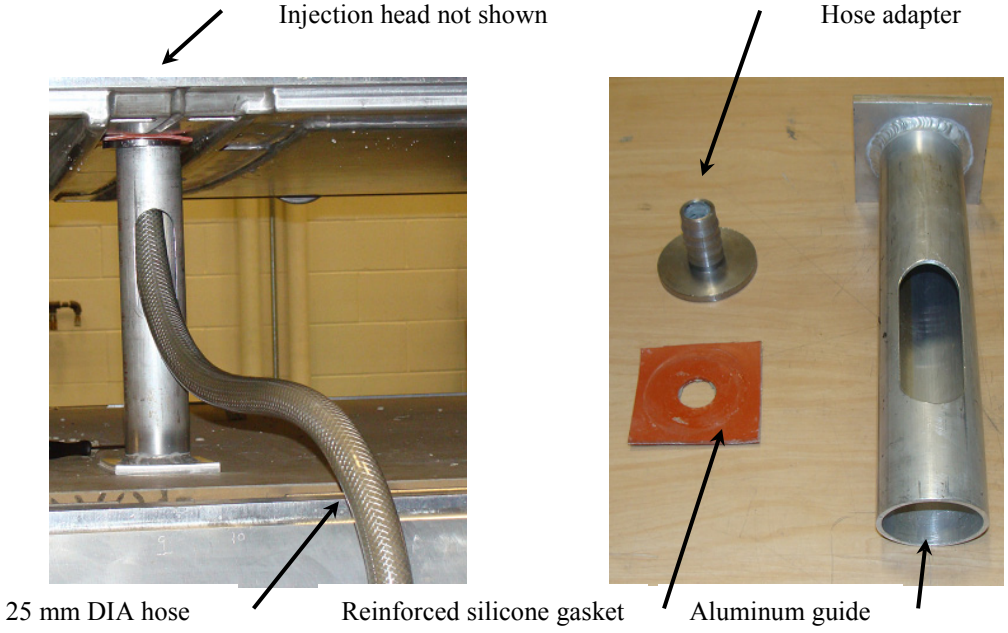


Figure 4-11: Components for direct hose injection into mould.

The lid of the characterization mould developed in this project has several novel features; the lid is designed with a diaphragm pressure transducer model DTMFB with a range from 0-10 bars. This transducer senses cavity vacuum as well as the pressure of the foam. As well there is a surface mounted Micromet impedance sensor. This sensor measures the changes in dipole mobility in the reacting foam identifying the gel point in the reaction. As well there is a type J thermocouple which is imbedded 25 mm into the foam. This thermocouple measures the exothermic behaviour of the foam. There is a second thermocouple that is used to measure the surface temperature of the foam. A sight glass window is used to make it possible to see the actual saturation event the polyurethane and fibreglass. Both sides of the lid are shown in Figure 4-12.

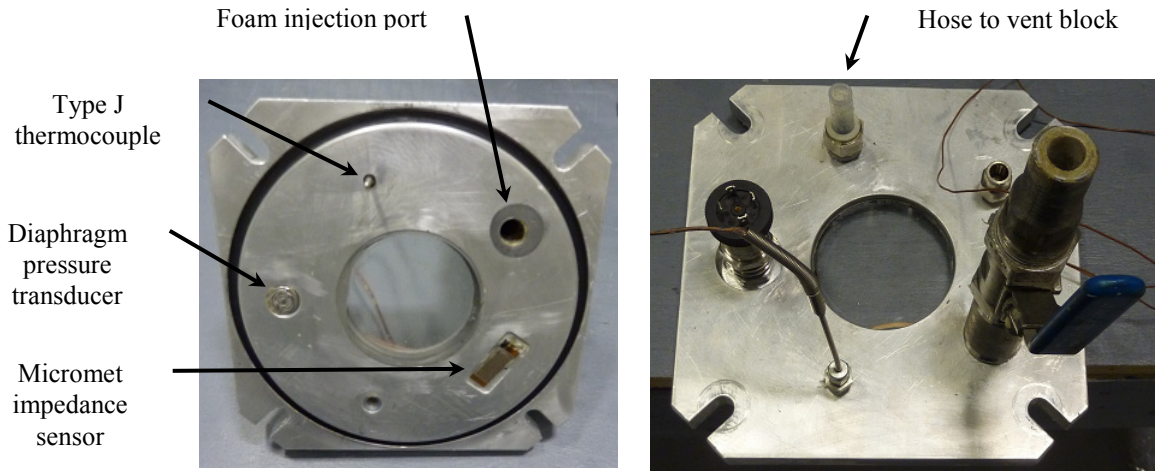


Figure 4-12: Instrumentation for the characterizing mould.

In parallel with the development of the characterizing mould a second Labview interface was developed for the moulding under pressure characterizing. The interface is shown in Figure 4-13.

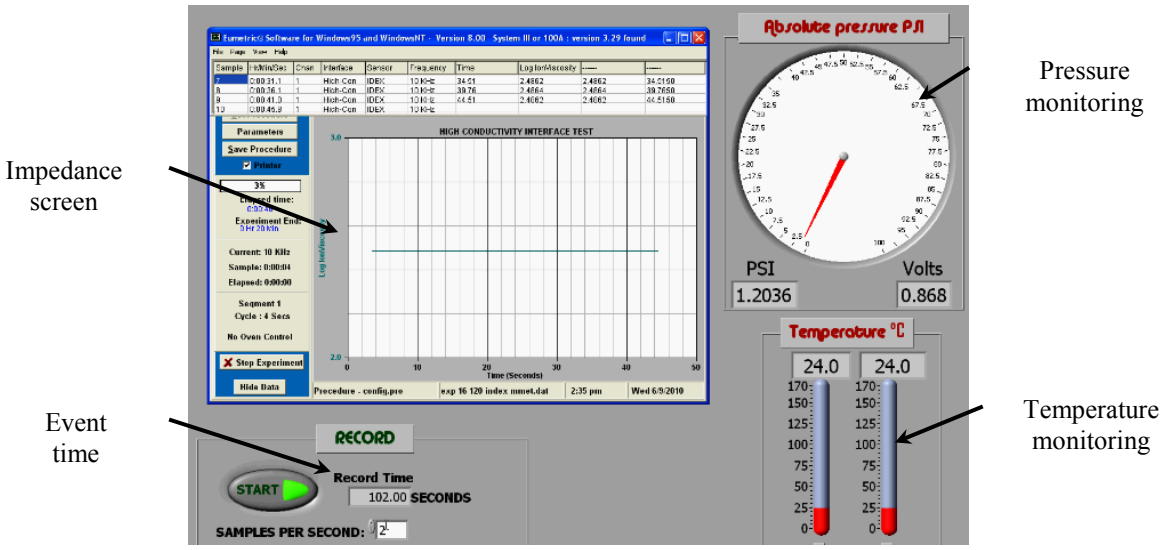


Figure 4-13: Second computer software interface developed in this work.

The objective of this characterizing system is to be able to visually confirm the actual saturation phenomenon in real time. As discussed earlier the log of the ion viscosity measured using the Micromet impedance sensor will be used to determine the gel point during the reaction. The actual pressure of the foam will be monitored throughout the reaction. As well the exothermic behaviour will be monitored. At the same time the start and stop of the fibre impregnation with the liquid polyurethane will be observed through the site glass window. An example of the measured data is shown in Figure 4-14.

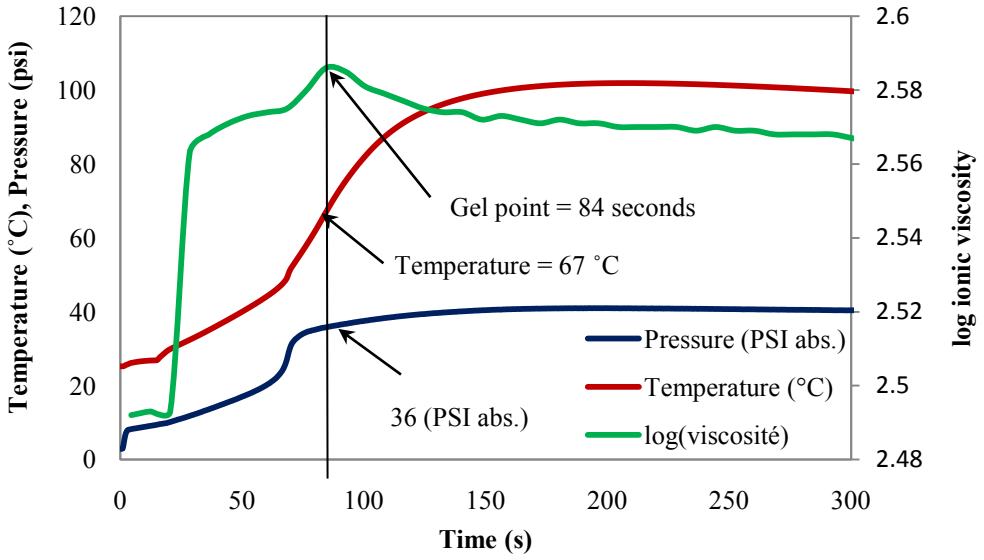


Figure 4-14: Results for characterizing tools; foaming under pressure.

With this mould it is possible to measure the foam pressure and temperature at the time of gelation. After gelation saturation and wetting of the fibres stops even though the pressure and temperature continue to increase. When optimizing the parameters of the foam it is possible to see significant shifts in the gel point, pressure at gel and temperature at gel. This can lead to improvements in the development of the skin and saturation of the fibres.

4.4.1 Injection procedure for the cylindrical characterization mould

The 9 L mould is first cleaned and three coats of mould release (Chem Trend PURA 16100) are applied to all of the surfaces in contact with the foam. The lid is also cleaned and waxed. Any remaining foam in the injection port is removed by drilling a hole using a 20 mm DIA drill bit. The gasket located in the ring must be cleaned and waxed each cycle. Next, a piece of engineered glass with an areal weight of 678 g/m^2 (20 oz/yd^2), measuring approximately 10 x 10 cm is bonded to the underside of the lid using two sided tape directly over the window. The lid is shown in Figure 4-9. The lid is then placed over the lower mould and the closure system is set in place and the bolts are torque to 41 N.m (30 ft.lbf). The hose adapter is cleaned and again, any remaining foam is removed by drilling a hole using the same 20 mm DIA drill bit. A 1m long piece of hose is attached to the hose holder and placed inside the aluminum guide shown in Figure 4-11. A silicone gasket is placed on top of the hose holder and the assembly is placed directly under the mix-head opening inside the large mould. The press is then closed and a pressure of 20 T is applied to the holder. The opposite end of the hose is attached to the lid of the mould. The venting system shown in Figure 4-10 is cleaned and a new 30 x 30 x 13 mm porous vent is placed inside and the bolts are tightened. All of the hoses are connected. The instrumentation is connected to the data acquisition systems and tests are performed.

Before resin injection, the atmosphere inside the mould was reduced to near full vacuum. The injection parameters were kept constant with the first set of experiments see Table 5-1. A moulded foam part with the glass fibres is shown in Figure 4-15.

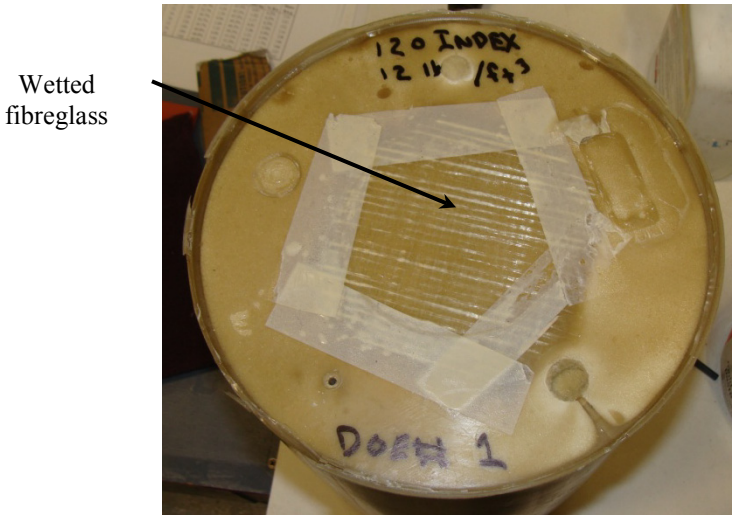


Figure 4-15: Example of a moulded with saturated fibres.

4.5 Foam injection into a three dimensional mould without fibres

In order to mould actual parts using this technology a multi-cavity panel mould was chosen as the surrogate mould. This mould has three cavities. The actual part is an automotive pick-up truck cover. This mould was manufactured by Decoma and sold to École Polytechnique de Montreal in 2007. As well, because of the size of this mould approximately 3 x 2.5 x 1 m high and weighing 5000 kg, it was set up in the 400 T Eagle press located in the Laboratory for Integrated Composite Manufacturing (LFIC) in St-Hubert. The mould and press are shown in Figure 4-16.

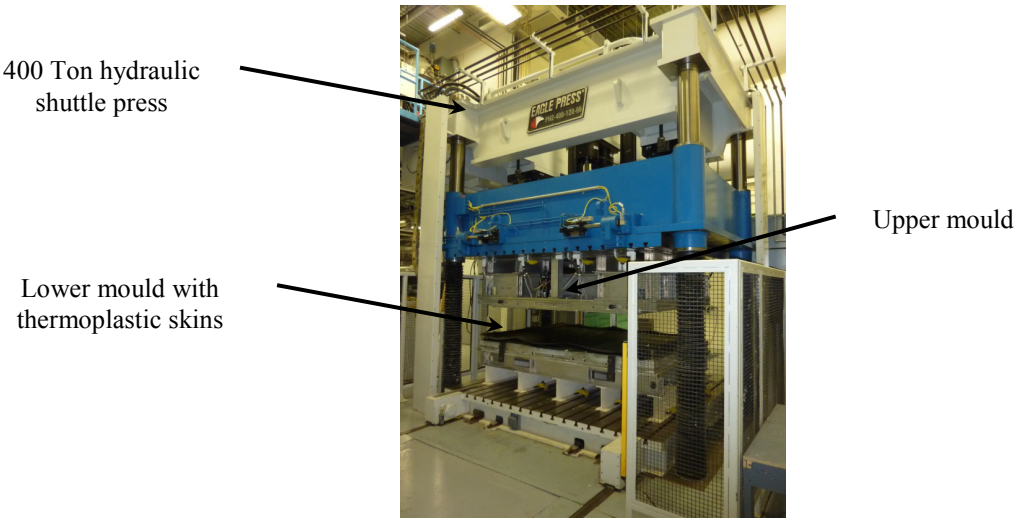


Figure 4-16: Three cavity panel mould located in the Eagle Press.

To get ready for this work a high pressure manifold was designed and installed making it possible to inject PUR resin directly into each of the three cavities shown in Figure 4-17.

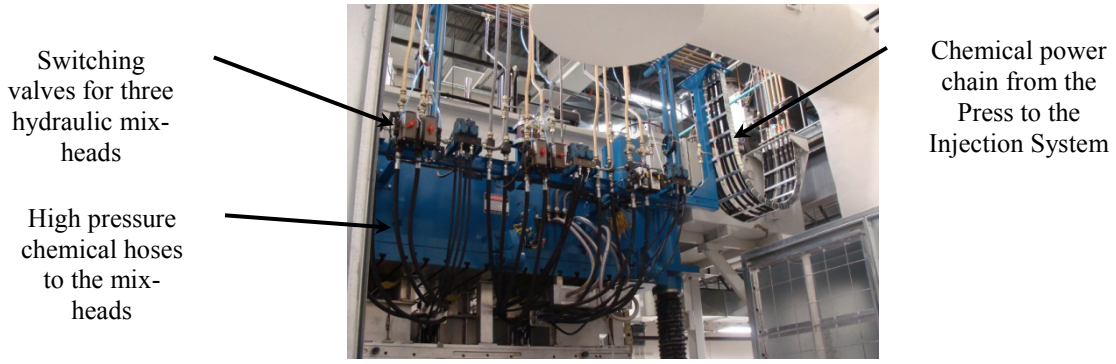


Figure 4-17: Installation of high pressure manifold from injection system to press.

Another contribution to this work was the design of a vacuum venting manifold for the three cavity mould. In order to inject the PUR into the individual cavities a venting system was conceived comprising of six solenoid control valves, and four pressure transducers. To control these valves modifications were made to the Allen-Bradley control program and the human-machine interaction panel (HMI) for the Eagle press. The changes to the Eagle press made it possible to control the valves individually during the process of injecting a part. A typical sequence is as follows: The bolster shuttles into the press and the press closes and applies tonnage, vacuum is applied to the thermoplastic skins to hold them in place using two valves. When the skin vacuum reaches 29 ”Hg, a valve opens to evacuate the air inside each of the cavities. When the set point is reached injection of the PUR can commence. After the third injection is completed, the cure timer starts. The opening sequence is as follows: First the vacuum (cavity vacuum) is released, then the skin vacuum for upper mould is closed and the air eject valve is opened, now the press is ready to open. Then the bolster shuttles to the demould area and the air eject valve on the lower mould opens. The new screen interface was developed in this work to control the valves is shown in Figure 4-18.

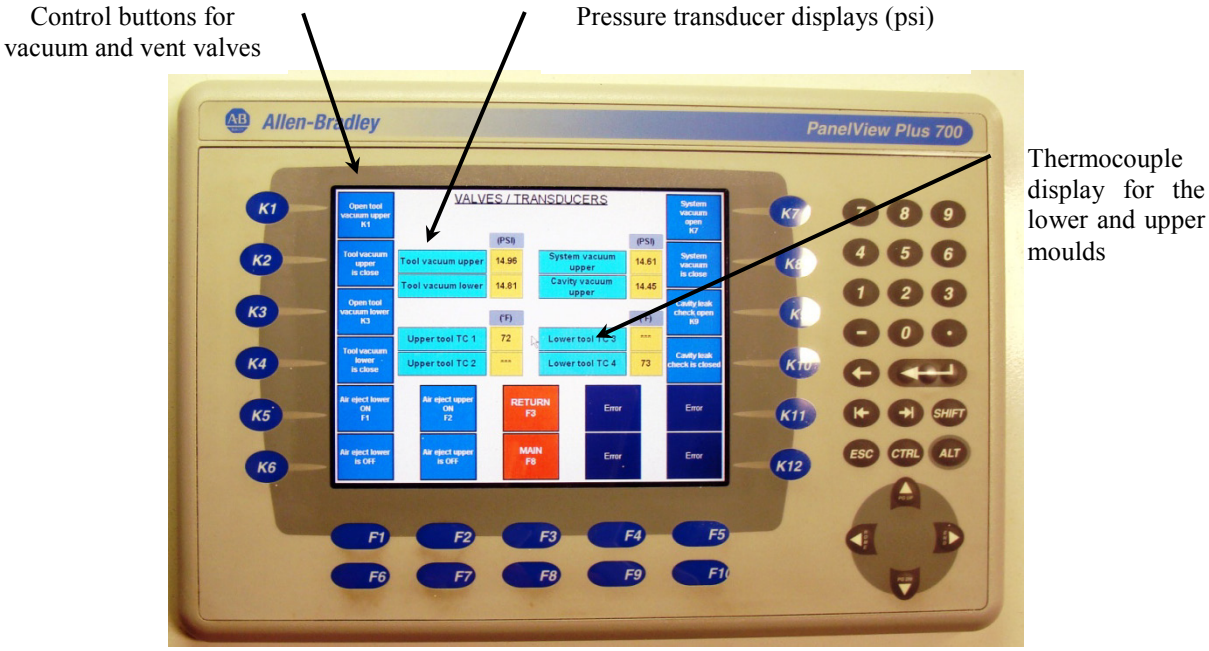


Figure 4-18: Screen developed for the 400 T press to control the vacuum system.

4.5.1 Description of the multi cavity panel mould

The multi-cavity mould used to fabricate the three dimensional panel parts is shown in Figures 4-19 and 4-20. The mould halves were made from machined aluminum billet (AL7075). The mould has integral heat lines and a vacuum box. Vacuum is used to hold the thermoplastic skins securely against the mould surfaces. Vacuum is communicated from a cavity below the surface of the mould, through a grid of 1.2 mm holes spaced approximately 100 mm apart. There is a 6.4 mm square seal profile cut into the upper mould. The square seal inserted in the groove is standard Buna N with a hardness of 70 Shore A. There is an opposing triangular groove in the lower mould that is used to locally deform the thermoplastic in the seal area. This makes it possible to achieve a high vacuum inside the mould. The PUR foam enters each of the three cavities using three gating features cut into the lower mould cavities. The fan gate is shown in Figure 4-21. This gating feature is cut into the lower mould; as well the same shape is also moulded into the outer skin. The foam flows through the cavity to the vent. A cross section of the part is shown in Figure 4-22.

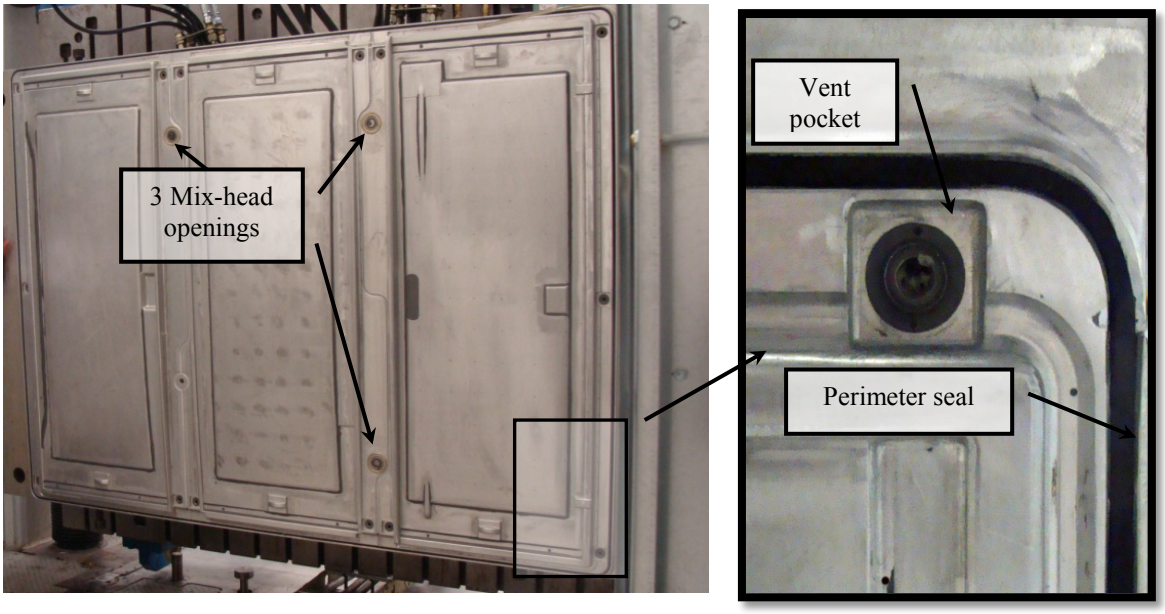


Figure 4-19: View of the upper mould in booked open position.

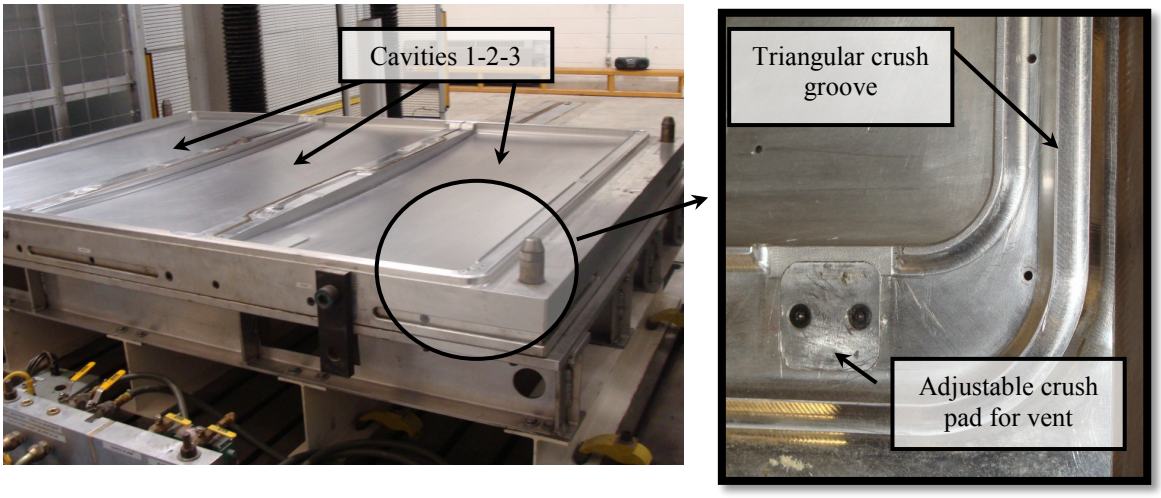


Figure 4-20: View of lower mould on shuttle outside of the press.

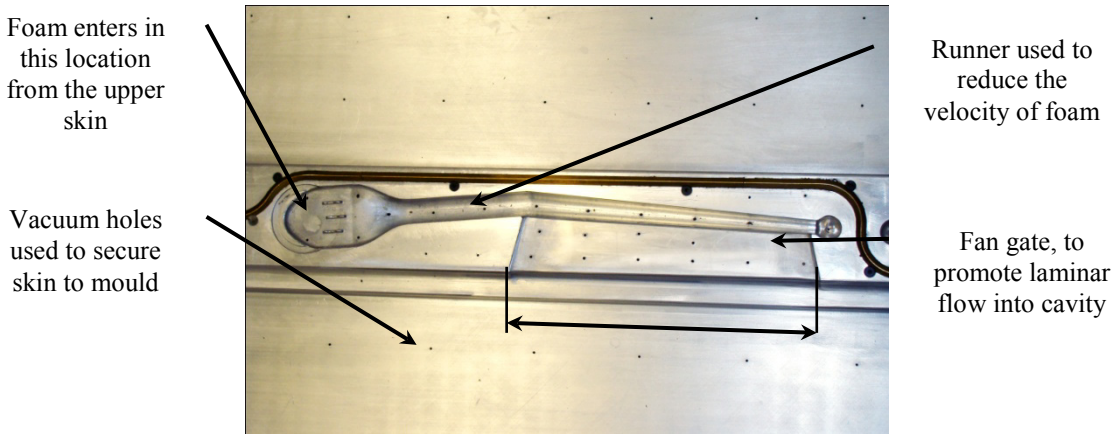


Figure 4-21 : Design of the RIM fan gate.

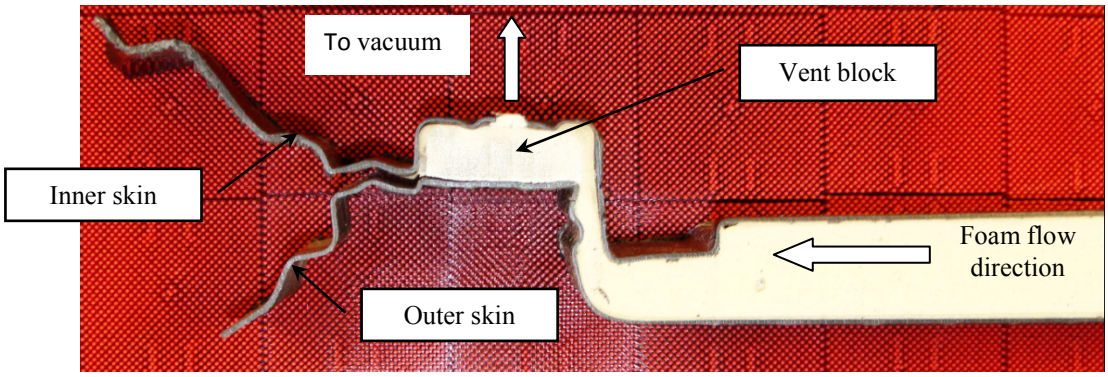


Figure 4-22 : Cross section of the sandwich part.

4.5.2 Thermoplastic skin preparation procedure

The inner and outer thermoplastic skins are shown in Figures 4-23 and 4-24. In order to mould the three dimensional part the thermoplastic skins are prepared as follows. First the inner and outer thermoplastic skins are cleaned using isopropyl alcohol (IPA). Then the Chem-Trend PURA 16100 mould release is sprayed on the inner surface of the thermoplastic skins. Next the outer skin is placed inside the lower mould. The inner skin (upper mould) requires additional preparation. First, fourteen 10 mm diameter holes are drilled in each of the vent pocket locations, then three 25 mm diameter holes are drilled through the skin in where the injection gates are located. Next fourteen vent blocks are placed into the vent pockets located around the cavities. Using high temperature hot melt adhesive the vents are bonded to the skins. This ensures the vents stay in place when the skin is turned upside down. Next the skin is placed over the outer skin already placed in the lower mould. Now the skins are ready for foam injection.

(a) (b)

Figure 4-23: Inner PC/ABS skin (a) textured show surface and (b) smooth foam surface.

(a) (b)

Figure 4-24 : Outer Acrylic capped PC/ABS skin (a) textured show surface, (b) smooth foam surface.

4.5.3 Injection Procedure for the multi cavity mould

After the thermoplastic skins are prepared as described above the mould is ready for injection. The two mould heaters must be turned on and set to their desired temperatures, typically around 35°C. There are temperature displays for both moulds visible on the HMI screen for the press as shown in Figure 4-18. Prior to injection the recipe for the PUR must be calculated and uploaded to the injection system control system. The pressures of each of the chemical components were be set to 7000 kPa. This is done by circulating the injection machine at high pressure and manually adjusting the orifices located on each side of the mix-head with a 6mm hex wrench. When the pressures are set the system is now ready.

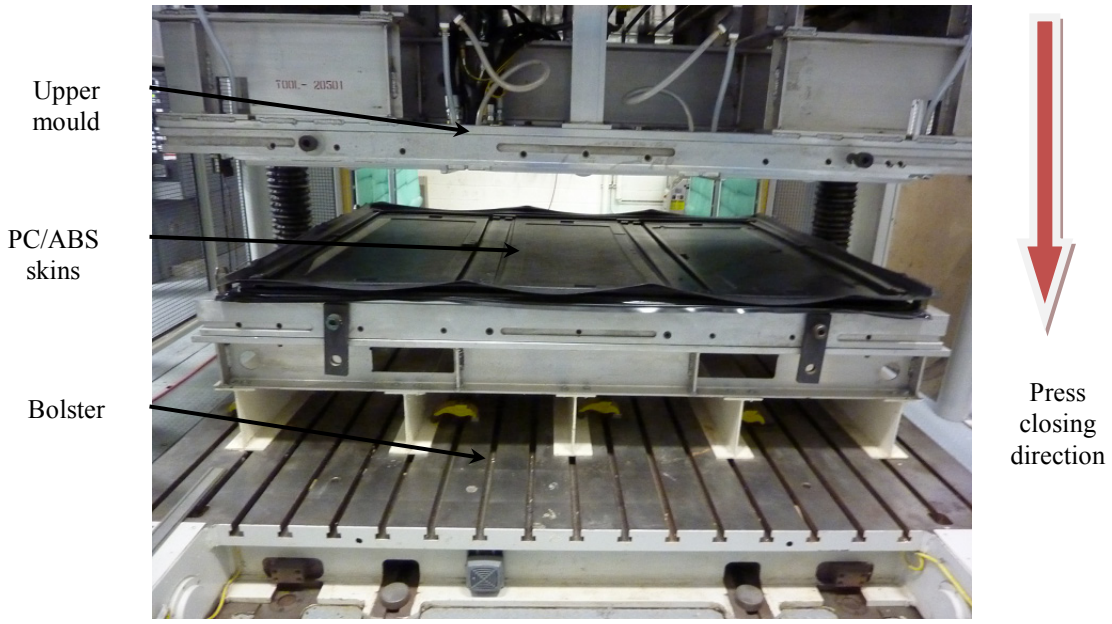


Figure 4-25: Press closing on thermoplastic skins just before resin injection.

The injection sequence starts by moving the bolster into the press followed by closing the mould and applying a closing force of approximately 200 T. Next the skin vacuum valve is turned on which holds the skins against the mould surface. Then the cavity vacuum value opens, which draws the air out of the cavities through the porous vents, when the pressure inside the mould cavity gets to 29 ”Hg. The injection sequence is started. Each mix head is injected sequentially using preset parameters. After the third mix-head has completed the injection the process cure timer is started. For the entire panel moulding trials, the cure time was set at 600 seconds. When the curing is complete, the vacuum valves are closed and the air eject valves are opened. The press is opened and the shuttle is moved to the demould position. Now the part is ready to be demoulded. See Figure 4-26.

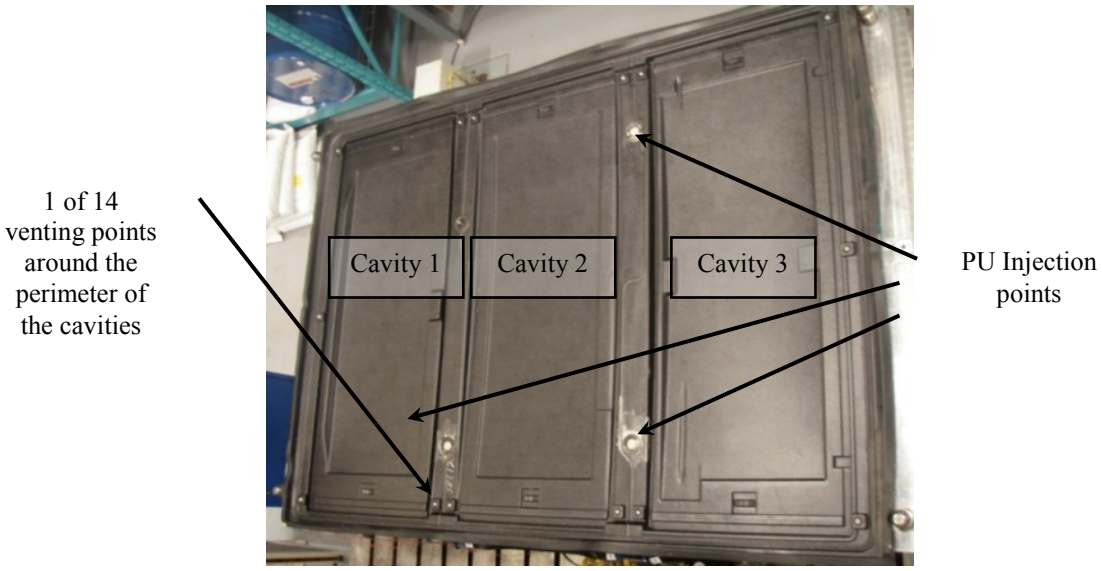


Figure 4-26: Top view of three cavity part after foam injection.

4.6 Foam injection into a three dimensional mould with fibres

The addition of the engineered fabric completes the product and significantly increases the mechanical properties. The challenge when moulding sandwich composites usually comes when the fibres are impregnated with resin. As described in Section 2.2 the novelty of this process comes from the fact that the core and laminate are formed in one step using the self skinning nature of the PUR foam. A challenge that exists is how to hold the engineered fibres in place in the mould where there is a void cavity. This was resolved by developing a pre-forming process that uses a UV adhesive to bond the engineered fabric to the thermoplastic the procedure is described below. The injection procedure is the same as described in Section 4.5.3.

4.6.1 Preforming the bi-directional fibreglass and thermoplastic skins

As described in 4.5.3 first the thermoplastic skins are cleaned with isopropyl alcohol (IPA). One hole is drilled through the skin to be used as a vacuum vent. Next 30 g of the UV binder CB601 is sprayed on the surface of the plastic skin with large 5 mm DIA droplets using a gravity fed Gelcoat spray gun (see Figure 2-17). Then the fibreglass mat is cut using the Lectra V2500 then it is placed over the sprayed skin. This procedure is repeated for the 3 cavities. Then sealing tape is applied to the perimeter of the part and a 5 mil thick polyethylene film sheet is placed over the entire surface and sealed. Vacuum is applied to the cavity using a suction cup located below the

pre-drilled hole. As the air is drawn out of the cavities the fibres begin to take the shape of the three dimensional part. Trace amounts of UV resin begin to saturate through the fibres. After a vacuum leak test the part is now ready for curing. The cart is moved into the UV tunnel and the drive pin is extended, the retractable vacuum hose is also fixed to the cart. The safety door is closed and the reset button on the UV control panel is activated, if there are no errors the beacon light will go out. Next the start button is pushed the beacon light will turn green and the cart is automatically drawn through the tunnel at a preset speed and distance from the lights. When the curing is completed the control system reverses the cart back to the start position. When the beacon light goes out it is safe to open the safety door and remove the cart. This procedure is repeated for both skins (inner and outer) as shown in the Figures 4-27 to 4-34.

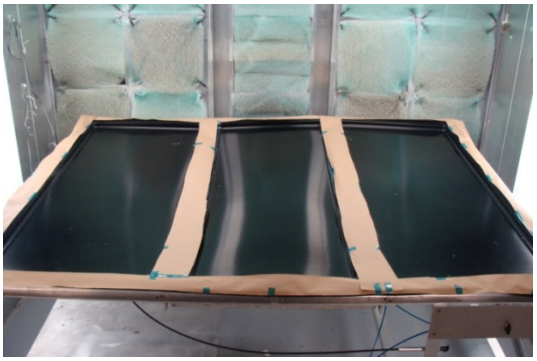


Figure 4-27: Inner skin with spray mask.

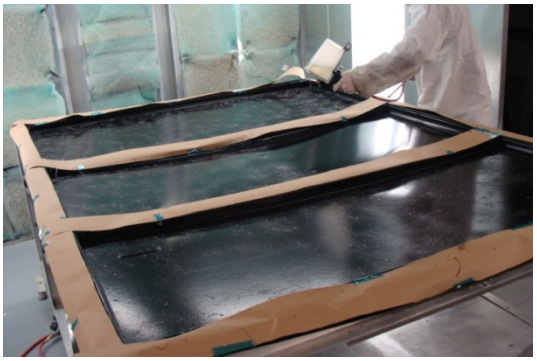


Figure 4-28: Spraying the UV binder.

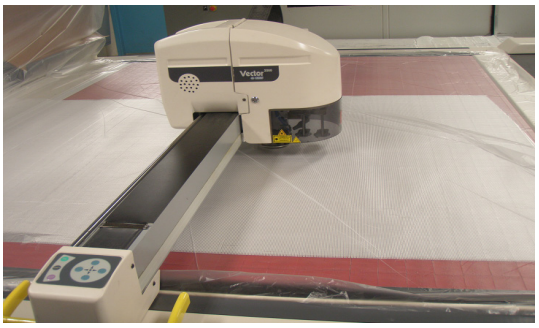


Figure 4-29 : Cutting fibreglass using the Lectra V2500.

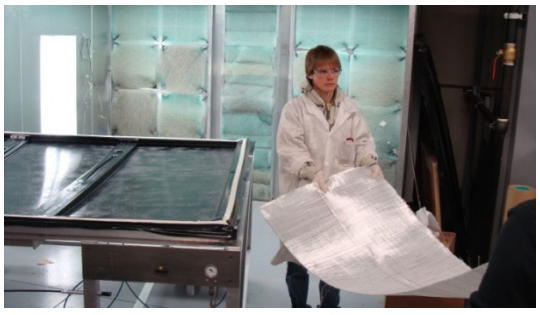


Figure 4-30 : Transferring fibres into skin.

Figure 4-31 : Vacuum bagging pre-form

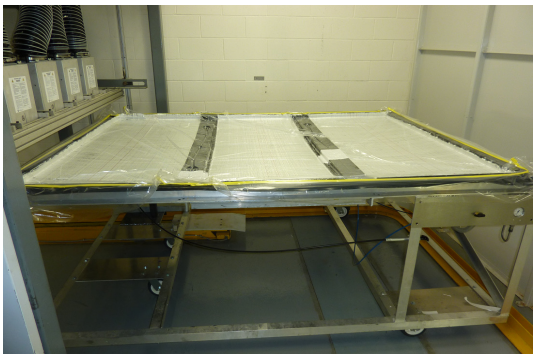


Figure 4-32 : Positioning cart in UV tunnel.

Figure 4-33 : UV tunnel with open safety door.

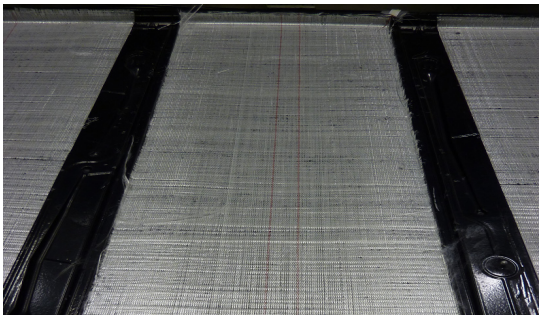


Figure 4-34 : Cured pre-form for inner skin.

CHAPTER 5 OPTIMIZATION OF THE RESIN FORMULATION

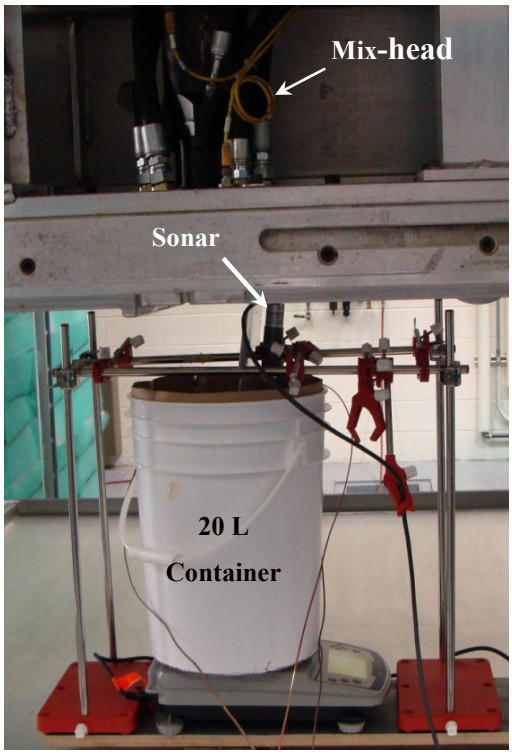
5.1 Introduction

In this section of the work, to optimize the PUR resin formulation, a series of four plans of experiments have been conducted. This study helped in understanding the foam formation mechanism and its relationship with the different resin components. In the experiments described in this section, the ratio of components in the resin was varied in order to link the mechanical properties to the resin formulation. The first plan of experiments focused on the behaviour of the polyurethane foam under conditions of free rise expansion. These tests aid in understanding some of the critical foaming characteristics such as the start of polymerization (cream), and the time when the reacting liquid turns into a solid (string gel) (see the foam formation stages in Figure 4-1). The second plan of experiments was completed in a closed cavity mould. Measurements of physical parameters were made in real time to understand the behaviour of the foam under pressure. A glass window in the mould made it possible to observe the filling time and saturation of reinforcing fibres in real time. The third plan of experiments was completed in a large panel mould using the manufacturing techniques described in chapter 4.5. A release agent was applied to the thermoplastic skins to prevent bonding with the foam. This made it possible to remove the thermoplastic skins after moulding in order to observe the foam formation and fibre impregnation. Flow related defects were also evaluated through visual observation. Samples taken in positions around the moulded panels were used to measure the compressive strength and density variability. Lastly, a fourth plan of experiments was conducted using the same panel mould. However, engineered fibreglass preforms were bonded to the thermoplastic skins in order to reinforce the sandwich composite. Mechanical properties of the sandwich structure, such as tensile strength, flexural strength, and facing shear stress were performed on samples. Some additional foam properties were also measured on this last experimental plan such as density and glass transition temperature.

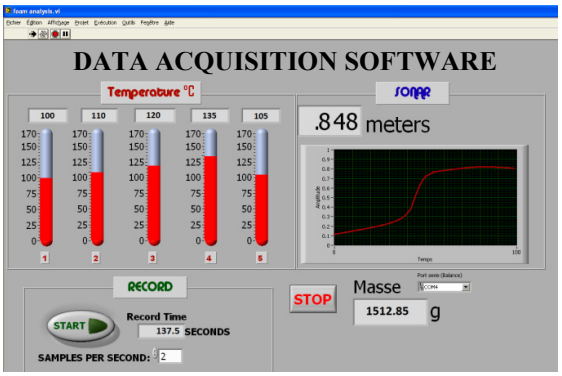
5.2 Foam free rise analysis

The analysis carried out in this stage of the research focused on determining the free rise behaviour and density for a rigid polyisocyanurate foam formulation with different stoichiometric proportions. The characterizing equipment used to conduct these tests was previously described

in section 4.3. The experimental setup is shown in Figure 4-4. The mixed resin was injected into a twenty litre container used to measure the free rise of the foam, see Figure 5-1(a). The rise profile was measured using a Senix® ToughSonic®/PC distance sensor. The temperature readings were made using type J thermocouples, and the gas losses were measured using a precision scale. Figure 5-1(b) shows the data acquisition software developed in Labview to measure the temperature, foam height and gas losses during foam formation. A picture of a typical moulded part is presented in Figure 5-1(c).



(a)



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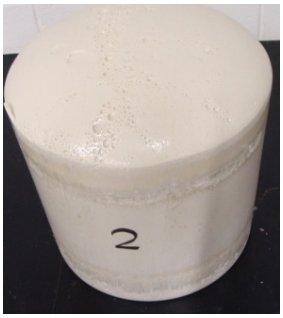


(c)

Figure 5-1: (a) Foam free rise apparatus, (b) data acquisition software and (c) moulded part.

In the first plan of experiments, a total of twelve injections were carried out using six different resin formulations, varying the isocyanate index from 110 to 160. For each injection the exothermic temperature was recorded at five positions vertically along the wall of the container at

50 mm increments and one in the bottom centre of the container 25 mm deep into the foam. The rise profile and weight loss were also recorded in time.

Table 5-1 lists the injection parameters used in the first plan of experiments. These parameters set for the injection system were held constant throughout the experiments to minimize variations between injections. The mixed polyol and isocyanate were held constant at 26°C. This temperature was set during previous tests. The flow rate was also kept constant at 1000 g/s total for the two components. This was also determined in earlier experiments where the resin flow rate was varied from 500 to 2000 g/s. Flow related effects were examined in the large panel mould (see the example shown in Figure 5-2).

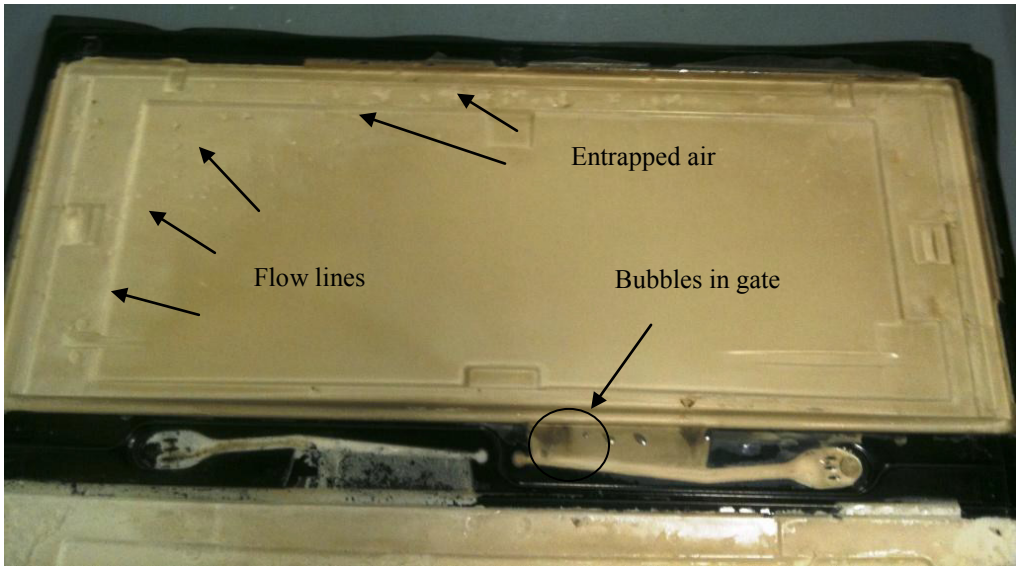


Figure 5-2 : Resin injection at a flow rate of 2000 g/s.

The impingement pressures were set at 7000 kPa after evaluating the foam mix quality. In this experiment it is desirable to keep the impingement pressures as low as possible to minimize the temperature increase that occurs when the resin flows through the orifices. In all of the tests for the first plan of experiments, the total mass injected was set at 1.25 kg. The control system for the Cannon A200 machine automatically calculates the desired flow rates of each component based on the desired flow rate and ratio of the components. The injection parameters on Table 5-1 are entered into the controller through an Allen Bradley user interface.

Table 5-1 : Injection parameters used for the first plan of experiments

Characteristic	Description	Value
Index (I)	Stoichiometric ratio = Ratio A/B Isocyanate / Resin	(NCO / OH)
σ_{pu}	Density of foam based on target shot weight	(kg/m3)
T_{polyol}	Polyol fluid temperature	26.67 ºC
T_{iso}	Isocyanate fluid temperature	26.67 ºC
Q_{pu}	Injection flow rate	1000 g/s
P_{poly}	Polyol impingement pressure	7000 kPa
P_{iso}	Isocyanate impingement pressure	7000 kPa
Total Mass	Injected wet weight of the foam chemicals	1.25 kg

Table 5-2 : Resin formulations used in the first plan of Experiments

Test	Index (NCO/OH)	Ratio (ISO/Poly)	Mass Polyol (g)	% Polyol	Mass ISO (g)	% ISO	Mass Blowing Agent (g)	% Blowing Agent
1	**110**	0.842	679	54.3	571	45.7	79	6.4
2	**120**	0.898	659	52.7	591	47.3	77	6.2
3	**130**	0.973	634	50.7	616	49.3	74	5.9
4	**140**	1.048	610	48.8	640	51.2	71	5.7
5	**150**	1.123	589	47.1	661	52.9	69	5.5
6	**160**	1.198	569	45.5	681	54.5	67	5.3

Table 5-2 summarizes the resin formulation of each of the six experiments. It can be seen that as the index drops the percentage of blowing agent increases. At an index of 110, the total percentage of blowing agent is 6.4% by weight. For an index of 160, the blowing agent reduces to 5.3%. The increase in blowing agent will lead to increased pressure in the foam; however it also leads to a drop in its mechanical properties. Therefore an optimization of the resin formulation is necessary to improve the final properties of the sandwich foam. Figure 5-3 shows the experimental results for an injection at an isocyanate index of 160. It can be seen that the start of polymerization occurred at 12 seconds after injection (see point (a) Cream time). The gelation occurred at 66 seconds (see point (b) String gel), and the foam surface became tack free at 88 seconds (see point (c) Tack free time). The foam rising behaviour shows a constant foaming rate until 60 seconds followed by a second acceleration. This acceleration occurs slightly ahead of the exothermic gradient at around 70 seconds. In the case where the foam is used to impregnate fibreglass reinforcing fabric, the foam movement prior to gelation will aid in fibre wetting. Therefore, it is desirable that the foam penetrates the fibres as early as possible before gelation to improve wetting results. This leads to 60 seconds of impregnation time before resin gelation. This time limit can be used to optimize the injection of the part by selecting the appropriate flow rate and gating strategy.

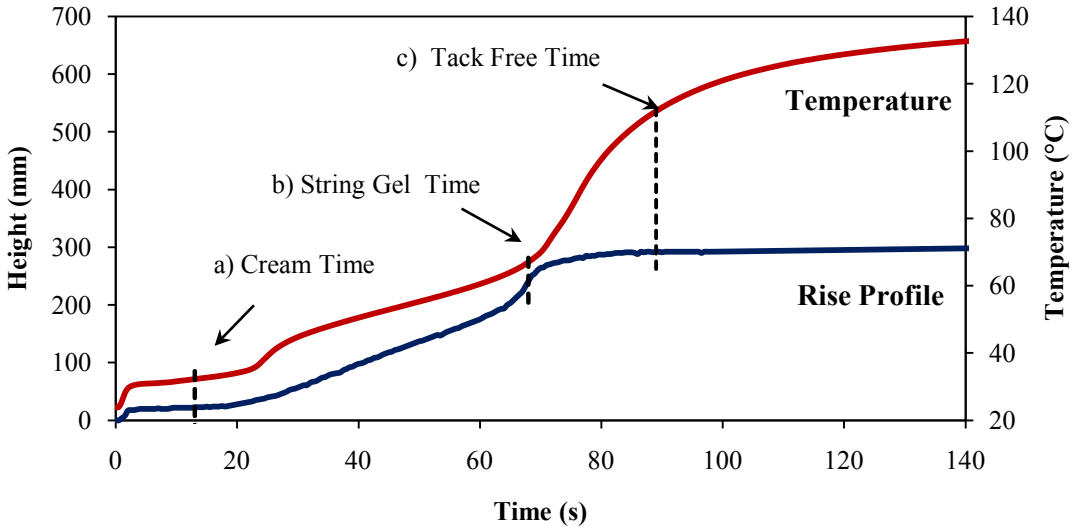


Figure 5-3 : Experimental results of a free rise test at isocyanate index of 160.

Figure 5-4 illustrates the experimental results for an injection carried out at an isocyanate index of 140. Comparing with Figure 5-3, it can be seen that while the beginning of polymerization occurs at the same time, decreasing the stoichiometric ratio speeds up the gel time to 62 seconds, and the tack free time to 82 seconds. The exothermic peak is also higher for the lower stoichiometric ratio, 147°C for 160 Index versus 140°C for the 140 Index, (not shown on the graphs). At the lower index the quantity of amine catalyst and HFC blowing agent increase while the quantity of isocyanate decreases. The increase in available catalyst accelerates the rates of reaction while the increase in the HFC blowing agent increases the mechanical blowing of the foam.

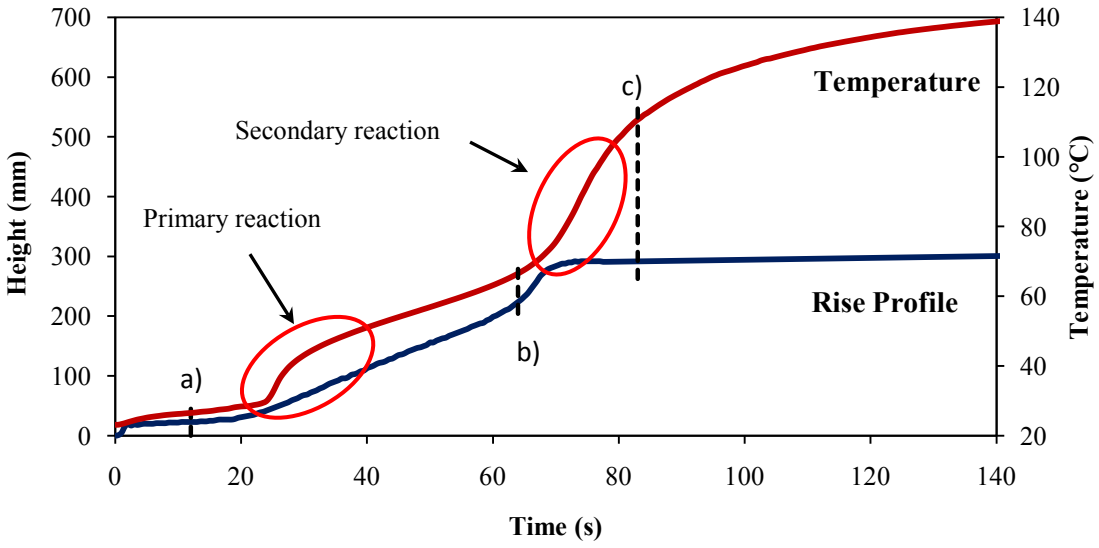


Figure 5-4 : Experimental results of a free rise test at isocyanate index of 140.

The twelve sample parts injected under different conditions were cut into smaller cylinders to measure the foam density according to ASTM D1622. The samples measured approximately 150 mm diameter x 40 mm thick, and were cut through the central axis of the part as shown in Figure 5-5.

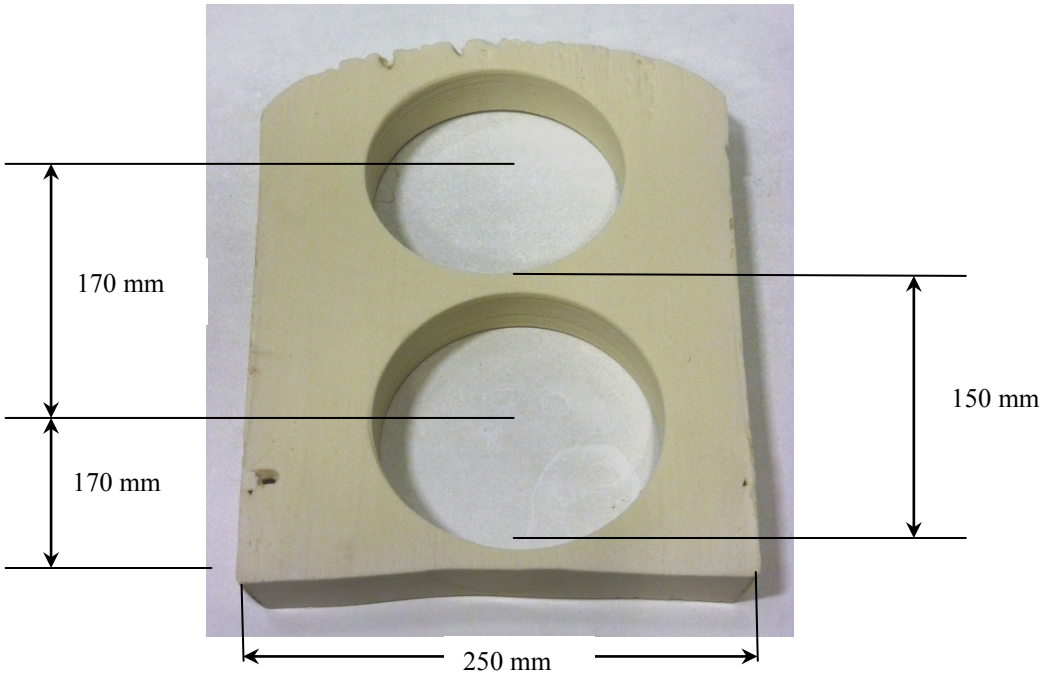


Figure 5-5 : Circular samples used to measure the foam density along the vertical axis.

This cutting plan was chosen to view potential density gradients along the vertical axis. As shown in Figure 5-6, the lowest foam density was achieved at an isocyanate index of 110. While increasing the stoichiometric proportions the caloric value in the foam increases; however, the percentage of blowing agent and percentage of primary and secondary catalysts decrease. This results in a decrease in blowing efficiency and a decrease in the developing pressure in the foam. As well, there is a delay in the gelation of the foam. In this particular process, where a fibrous reinforcement is impregnated by the collapsing foam, resin pressure and viscosity become important to enable the wetting phenomena. If resin gelation occurs too early in the process, the fibrous reinforcement will not be properly impregnated. Reducing the stoichiometric proportions increases the foam pressure in the foam but speeds up the cure reaction. Mechanical properties of the polyisocyanurate foam also decrease with decreasing stoichiometric proportions, partly due to a plasticizing effect caused by the HFC blowing agent. Optimizing the foam formulation becomes then a key part of the process, since maximizing the stoichiometric ratio will lead to better foam properties, but will increase the complexity of the fibre impregnation process. Figure 5-6 illustrates the effect changing the Index has on the density of the foam. As described earlier

in this section as the index drops the percentage of blowing agent increases, this additional HFC material assists the foam in expanding under atmospheric pressure. The percentage of blowing agent in the part drops 17% when the index goes from 110 to 160. For the parts produced in this study the measured density drops up to 12% when increasing the isocyanate to 160. From the observations in Figure 5-6, two statements are apparent: the first is as the index increases the variations in density within the part increases. This suggests that the foam is more unstable resulting in a higher degree of irregularity in the foam. The other observation is that at lower indices ranging from 110 to 120, there is a loss of blowing efficiency in the foam. It is possible that at low indices the diffusion of the HFC into the foam is disturbed by improper mixing, most likely due to the orifice sizing in the mix-head.

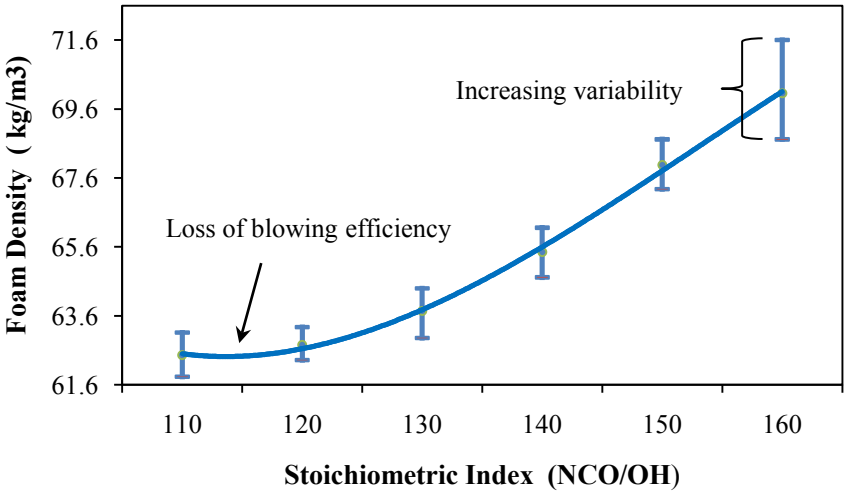


Figure 5-6 : Results of the free rise density characterization.

It should be noted that the free rise foam density is much lower than the density needed to fill the mould. Attempting to fill a complex mould with the same target density achieved in a free rise experiment would result in a part that may only fill half of the closed cavity. This is due to frictional resistance and back pressure created inside the closed mould during filling. In order to assess foam filling capability, the amount of over packing the foam should be determined. The pressure in the mould is dependent on the degree of over packing *E*, defined as [42]:

$$E = \frac{Required\ foam\ density}{Free\ rise\ foam\ density} \tag{5-1}$$

The degree of over packing increases pressure making it easier to fill the mould. In preliminary filling experiments it was observed that the minimum filling density was around 160 kg/m^3. To make the next plan of experiment robust and facilitate the fibre wetting, the degree of over packing *E* values has to be between three and four. Therefore, the next set of experiments will be run at moulding densities from 192 kg/m^3 to 256 kg/m^3.

5.3 Analysis of resin foaming under pressure

The objective of this second analysis was to understand the dynamic viscosity, pressure development and exothermic reaction that take place during foaming in a closed mould. This study was carried out using the closed mould described in section 4.4.

Before resin injection, the atmosphere inside the mould was reduced to near full vacuum. A moulded foam part with the glass fibres is shown in Figure 4-15.

A two factor three level plan of experiments was conducted. The factors studied were the isocyanate index (120–130–140) and foam density (192–224–256 kg/m^3). To follow the resin viscosity behaviour during foaming, the changes in the ionic viscosity were monitored. There has been considerable work on in-situ monitoring of matrix properties during cure using electrical methods such as dielectric sensing [43]. Additional measurements included real time pressure and temperature recording. Also, physical measurements on the moulded parts included density, skin thickness and laminate thickness.

The processing parameters were the same as the first plan of experiments as described in Table 5-1. The range for the stoichiometric ratio was reduced from the first plan of experiments between 120 and 140. Also, target densities varied between 192 and 256 kg/m^3 as shown in Table 5-3. The plan of experiments consists of nine injections carried out at different isocyanate indices and foam densities. Table 5-3 describes the moulding parameters used in the second analysis. For the lower density and isocyanate index (192 kg/m^3 and 120 Index) there was a total of 6.2% of blowing agent by total weight in the foam. For the higher density and isocyanate index (256 kg/m^3 and 140 Index), the blowing agent was reduced overall to 5.7% by total weight in the foam. This variation in the resin formulation has an impact on the foam behaviour, fibre impregnation and viscosity rise.

Table 5-3 : Injected resin volumes in the second plan of experiments, to obtain the desired foam density.

Mould volume (L)	Target density (kg/m^3)	Resin Shot size (kg)
9.5	192	1.85
9.5	224	2.15
9.5	256	2.46

Table 5-4 : Moulding parameters for the second plan of experiments on closed mould conditions.

Part	Density (kg/m^3)	ISO Index (NCO/OH)	Polyol (%)	Mass Polyol (kg0	ISO (%)	Mass ISO (kg)	Blowing Agent (%)	Mass Blowing Agent (g)
1	192	120	52.7	0.97	47.3	0.87	6.2	114
2	224	120	52.7	1.14	47.3	1.02	6.2	133
3	256	120	52.7	1.30	47.3	1.17	6.2	152
4	192	130	50.7	0.94	49.3	0.91	5.9	110
5	224	130	50.7	1.09	49.3	1.06	5.9	128
6	256	130	50.7	1.25	49.3	1.21	5.9	146
7	192	140	48.8	0.90	51.2	0.95	5.7	106
8	224	140	48.8	1.05	51.2	1.10	5.7	123
9	256	140	48.8	1.20	51.2	1.26	5.7	141

As shown in Figures 5-7 and 5-8, significant changes in the foam behaviour were observed when varying the resin formulation. At higher index and higher density (see Figure 5-8), the gel point is delayed 8 seconds, while pressure is increased by 71 kPa and temperature of reacting foam is 19°C higher at gel. These conditions result in changes in the foam morphology and skin thickness as shown in Figure 5-9. Injecting at low index and low density leads to coarse foam cells. This is mainly due to the excess in blowing agent and lower exothermic reaction of the mix. Injecting at the higher index and higher density, results in more uniform and fine foam cells and a thicker foam skin. This improves fibre impregnation and mechanical properties of the sandwich composite.

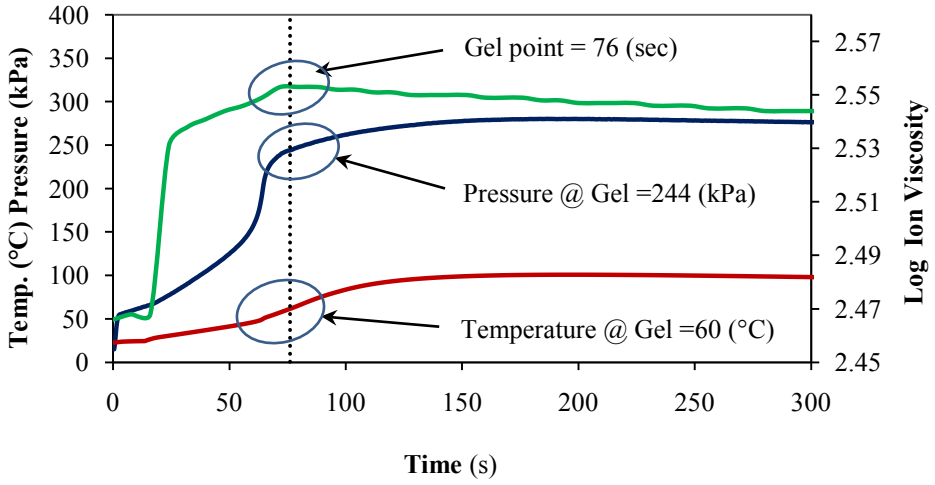


Figure 5-7 : Results of the injection at an Index 120 and density of 192 kg/m^3.

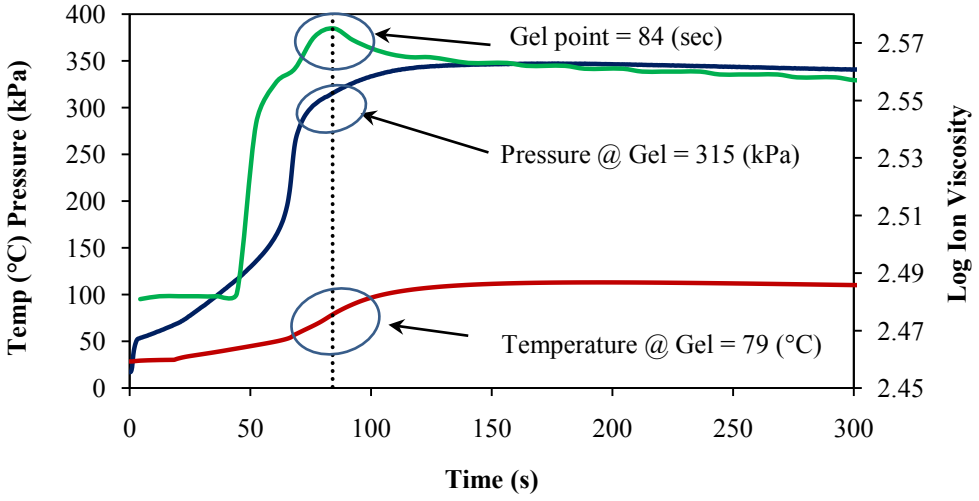
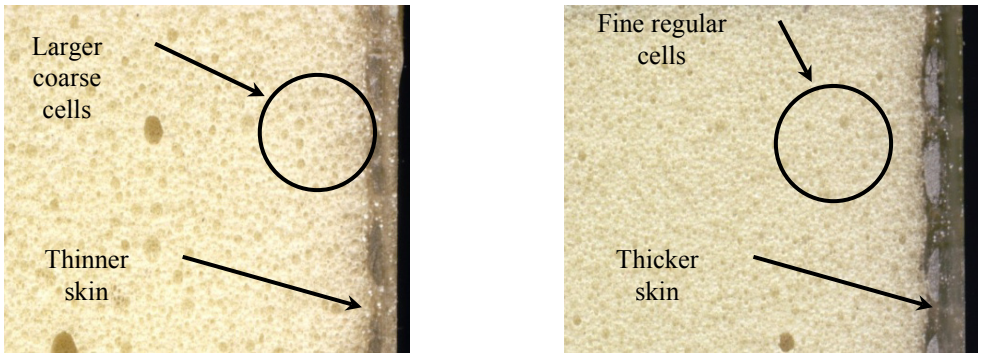


Figure 5-8 : Results of the injection at an Index 140 and density of 256 kg/m^3.



(a) (b)

Figure 5-9: (a) Foam observations at Index 120 and density of 192 kg/m3 and (b) at Index140 and density of 256 kg/m3.

The results of the fibre impregnation in the second plan of experiments are visualized in Figure 5-10. The numbers shown in the boxes correspond to the individual trials in the plan of experiments. All of the results are summarized in Table 5-5. These results indicate that the index effect is less significant than the density effect. The best wetting was observed at mid point conditions where the index was 130 and the density 224 kg/m^3. For this experiment the pressure at gel was measured at 275 kPa. The images show that the saturation of the fibreglass improved by increasing the density of the foam. For the high density cases (i.e. trials 3, 6 and 9), varying the isocyanate index did not have an important influence in the visible wetting of the fibres. This suggests that there was not sufficient blowing agent present to create the fibre wetting phenomena which resulted in a peak pressure greater than 300 kPa as shown in Table 5-5. In the left column where the density is constant at 192 kg/m^3 and the index values range from 120 to 140; the fibre saturation was poor and the resulting skin thickness was low at around 1.1 to 1.3 mm as shown in Table 5-5 (see trials 1, 4 and 7). At this density the pressure prior to gelation is insufficient to wet out the fibres measured at 244 kPa for the 120 index part and 225 kPa for the 140 index part. This drop in pressure occurred because the percentage of blowing agent and catalysts decreased as the index increased. In order to develop the best sandwich composite, the properties of the laminate and the foam must be optimized together. Increasing the index improves the mechanical properties of the foam but make it more difficult to wet out the fibres and increasing the density add weight and cost to the final part.

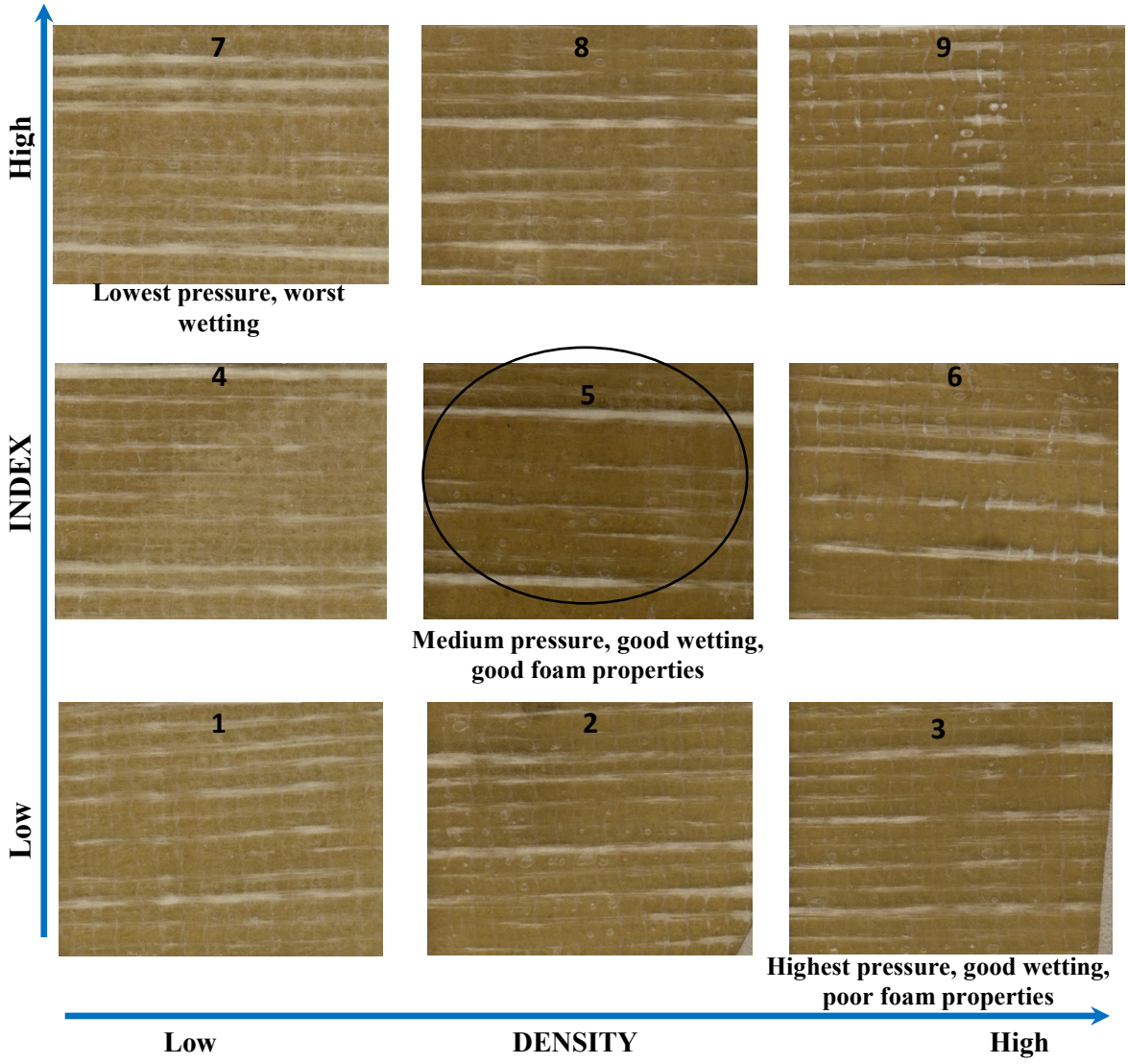


Figure 5-10: Surface appearance of foam impregnated glass fibres, Index 120 to 140 and density 192 to 256 kg/m^3.

Table 5-5 : Results from experiments of foaming under pressure.

Trial	1	2	3	4	5	6	7	8	9
INDEX (NCO/OH)	**120**	**120**	**120**	**130**	**130**	**130**	**140**	**140**	**140**
Density (kg/m^3)	**192**	**224**	**256**	**192**	**224**	**256**	**192**	**224**	**256**
Final weight (g)	1875	2189	2510	1880	**2179**	2481	1892	2170	2501
Gel time (s)	76	80	84	84	**82**	88	76	92	84
Pressure at gel (kPa)	243.9	289.9	340.8	246.6	**274.5**	319.8	224.8	271.7	315.4
Pressure maximum (kPa)	280.4	332.6	379.1	282.8	**311.2**	352.8	263.8	305.2	347.3
Temp. at gel (ºC)	61.5	65.1	71.0	66.5	**68.3**	76.1	59.7	69.9	78.6
Temp. maximum (ºC)	100.9	105.0	111.7	101.9	**106.3**	110.5	103.9	103.9	113.1
Skin thickness (mm)	0.76	0.76	0.76	0.67	**0.80**	0.76	0.59	0.72	0.74
Laminate thickness (mm)	1.12	1.30	1.13	1.23	**1.46**	1.26	1.10	1.26	1.27

Table 5-5 summarizes some additional measurements taken during this second plan of experiments, such as, the maximum pressure in the foam, the peak temperature and the thickness of the skin adjacent to the surface of the mould. There is a large difference in the foam pressure across this plan of experiments. Since the pressure is a function of the quantity of blowing agent and the exothermic peak, it was seen that the maximum pressure was measured at 263.8 kPa for trial 7 (i.e. high index and low density) to 379.1 kPa for trial 3 (i.e. low index and high density). This represents a 43% increase in peak pressure. For the same two trials, the peak temperature increased from 103.9ºC to 111.7ºC. The developed skin in the areas where no fibreglass was present was measured at 0.59 mm for trial 7 compared to 0.76 mm for trial 3. An increase in thickness was expected because of the pressure and temperature differences described above. The laminate thickness followed a similar trend going from 1.1 mm for trial 7 to 1.13 mm for trial 3. However, skin thickness of trial 3 was not the maximum observed, suggesting that peak pressure

is not the only promoter affecting cell collapse and fibre wet out. The optimal formulation was obtained for a medium index and foam density (i.e. trial 5). In Analysis of PUR foam moulded in a panel mould Table 5-5, the fifth column corresponds to the part shown in the centre of Figure 5-10. This part exhibited improved moulding results. In this case the pressure at gel was measured at 274.5 kPa while the temperature at gel was 106.3ºC. The resulting thickness of the laminate and skin were 1.46 and 0.8 mm respectively. These were both higher than the other trials. It can then be concluded that medium pressure and peak temperature lead to the best moulding results. This condition was obtained with a resin formulation containing a foam density of 274 kg/m3, and isocyanate index of 130 and a blowing agent of 5.9%.

5.4 Analysis of PU foam in a panel mould

The third plan of experiments focused on measuring the mechanical properties of the polyurethane foam moulded in a three dimensional part. This experiment investigated the impact on mechanical properties of the two main parameters previously studied, the isocyanate index and the foam density. Also, a third parameter was included in this experiment, the mould temperature. A total of fifteen injections were carried out using two levels of isocyanate index (120 and 140), three levels of density (192, 224 and 256 kg/m^3) and two levels of mould temperature (35 and 40ºC). The polyurethane resin was injected directly into the mould cavity using the Cannon A200 foam injection machine and FPL-24 mix-heads described in chapter 4. A picture of the moulding unit is shown in Figure 5-11. The mould is clamped with a 400 Ton hydraulic press. The cavity of the mould was conceived to manufacture three component panels at each injection. So to do so, three PUR resin mix-heads were installed on the upper mould which was clamped to the upper platen of the hydraulic press. The three mix-heads (resin mixers) are connected to the injection gates of the mould cavities.

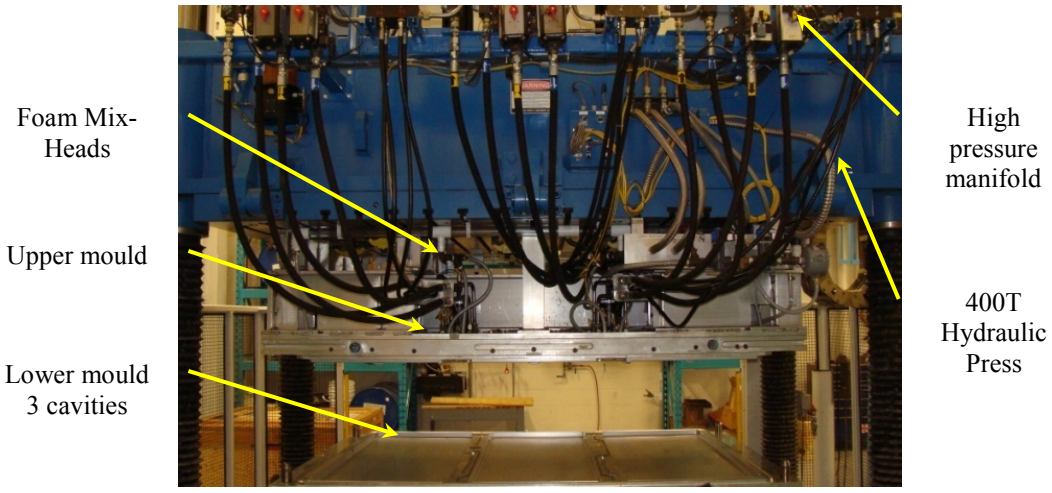


Figure 5-11: Panel mould mounted in hydraulic press.

The injection parameters were the same as in the previous studies (see Table 5-1). The manufacturing procedure is described in Section 4.5.3. In these experiments, a demoulding agent was projected on the thermoplastic skins to avoid bonding of the foam to the skins. After demoulding the part, the thermoplastic skins were then easily removed. This made it possible to analyse the foam formation along the entire surface of the part. Also, in these experiments no fibrous reinforcement was used, since the main objective of this study is to analyse the foam formation in a 3D part. Two thermocouples were placed inside the mould cavities at the two outermost vent locations as shown in Figure 5-12. The foam was injected sequentially into each of the cavities; first part 1 followed by part 2 and 3. The parts were then allowed to cool before demoulding.

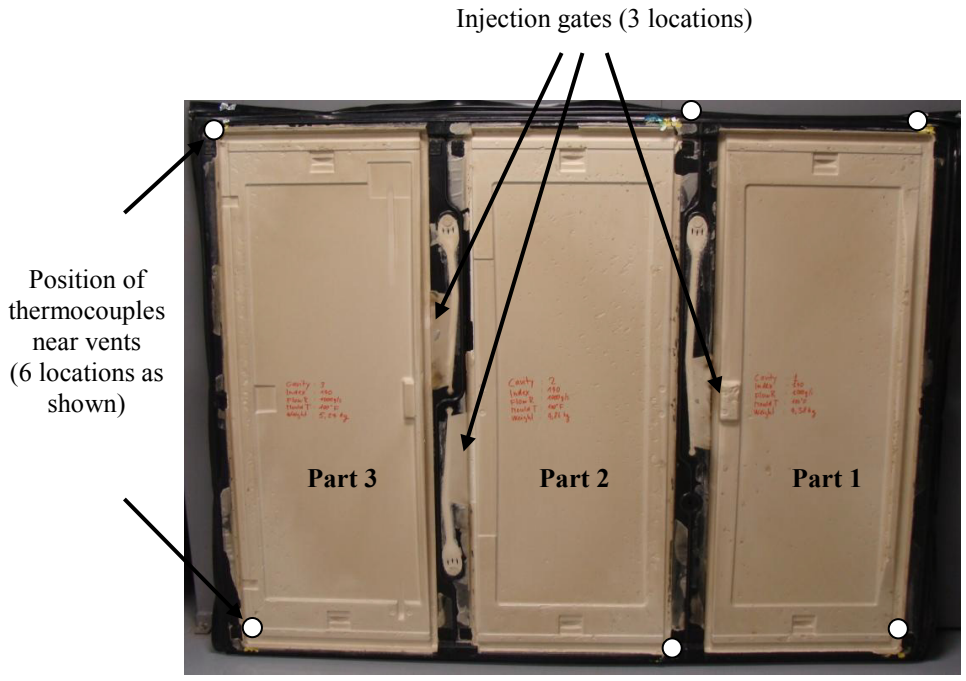


Figure 5-12 : Example of a 3D foam panel without its thermoplastic skin.

The main difference with this experiment over the second plan of experiments, which consisted in moulding a part in a closed cylindrical container, is that the three cavity mould is thermally controlled using heated water circulation. The foam is injected into two facing thermoplastic skins which are then removed after demoulding.

The mould temperature plays an important role in the formation of the polyurethane foam as well as in the creation of the integral foam skin next to the surface of the mould. The mould heating influences the reaction rate of the PUR and the filling of the cavity. If the PUR reaction is too fast (blowing reaction) there can be flow related defects in the part. For example, if there is a geometric feature in the part, the speed of the foam moving across the feature may cause a shadow on the low pressure side resulting in a void or knit line in the part. If the PUR reacts too slowly, mould filling may be incomplete and density of the foam will not be homogeneous throughout the part. Lastly, if the mould is too cold and doesn't provide enough energy to the PUR, the reaction will be incomplete and the mechanical properties will be adversely affected. Therefore optimizing moulding parameters is crucial for this foaming process. In this work, to improve the process for moulding this real part, a set of 12 injection conditions were experimentally evaluated. The moulding parameters used in this third plan of experiments are listed in Table 5-6.

Table 5-6 : Experimental plan used to study the foaming behaviour in a 3D mould.

	Part cavity	Trial	Density (kg/m^3)	ISO Index	Mould Temp (°C)	Ratio (ISO/ Polyol)	Weight (Kg)
Ex1	1	1	192	120	35	0.898	4.99
	2	2	224	120	35	0.898	5.55
	3	3	256	140	35	1.048	6.17
Ex2	1	4	192	140	35	1.048	4.99
	2	5	224	120	35	0.898	5.55
	3	6	256	120	35	0.898	6.17
Ex3	1	7	192	140	40.6	1.048	4.99
	2	8	224	140	40.6	1.048	5.55
	3	9	256	120	40.6	0.898	6.17
Ex4	1	10	192	120	40.6	0.898	4.99
	2	11	224	140	40.6	1.048	5.55
	3	12	256	140	40.6	1.048	6.17

As shown in Table 5-6, there were four individual setups, (Ex1 to Ex4), where three injections were completed consecutively using the three cavity mould. This nomenclature was chosen because the three cavities are held together is a single set of thermoplastic skins as shown in Figure 5-12.

In this study, three key foam properties were examined: the maximum compressive strength, the compressive modulus and the glass transition temperature (*Tg*) and density variation. A total of twelve parts were moulded according to the parameters exposed in Table 5-6. For each of these

parts, foam samples were cut to study their thermo-mechanical properties. A total of six samples were taken from each part following the resin flow directions as depicted in Figure 5-13. The variability of the density around the part is shown in Figure 5-14.

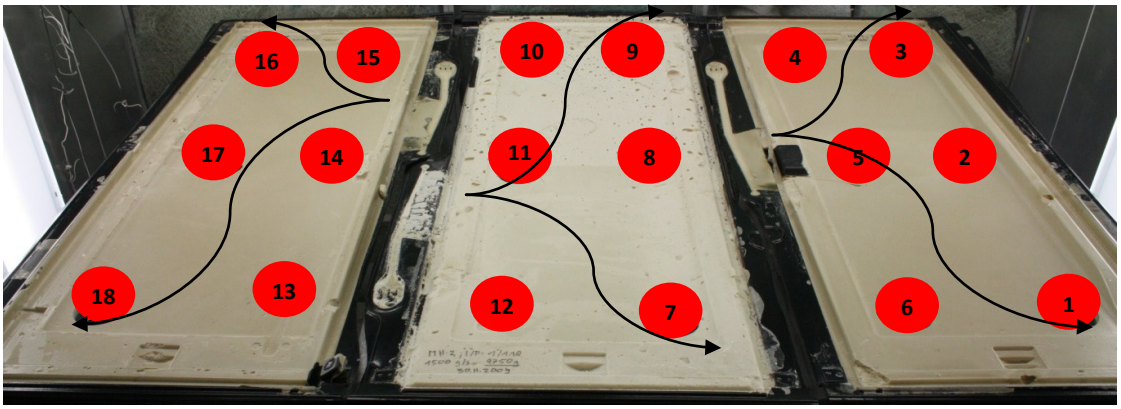


Figure 5-13 : Positions of foam samples taken across the part: Arrows indicate the foam flow direction from the gate to the vents.

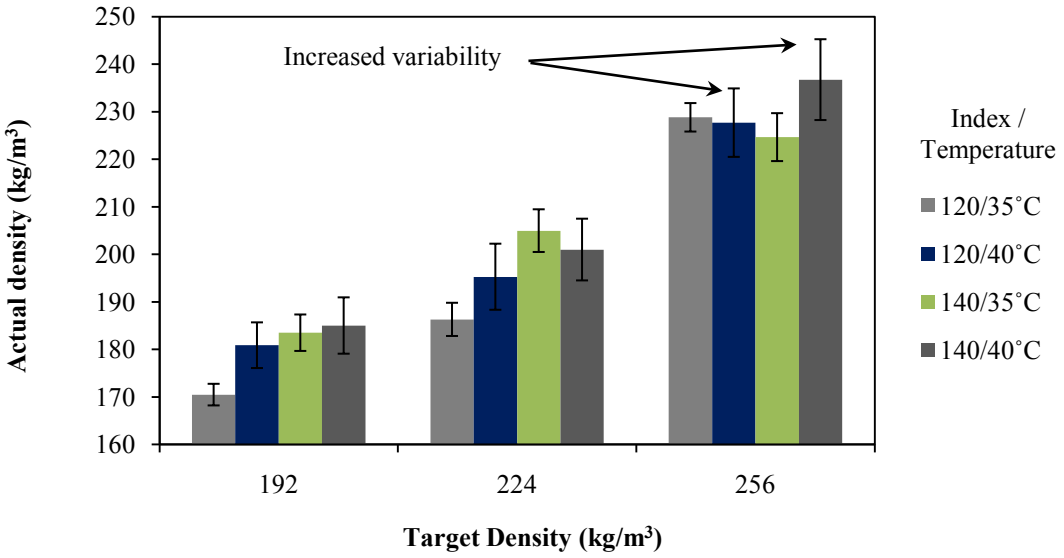


Figure 5-14 : Results of the density analysis for three dimensional parts at different isocyanate indices and foam densities.

The variation in density suggests that the foam is having difficulty filling the mould. This can be caused due to long flow paths. Also, if the resin builds viscosity quickly there can be increased friction during filling resulting in increased variability. It can be seen in Figure 5-14 that the higher moulding temperature (40°C) exhibits a more variability in the density around the part. Although the mechanical properties improve with increased temperature, the flow of the foam

changes which results in the observed high variability in the density. For this reason in the next plan of experiments the temperature range will be set to 37.5°C in order to minimize reduction of the foam properties while optimizing the flowing and filling behaviour.

The compression tests were completed using a 100 KN Instron® mechanical tester according to the ASTM D1621 standard, (see Figures 5-15 and 5-16)

Figure 5-15 : Instron® test machine.

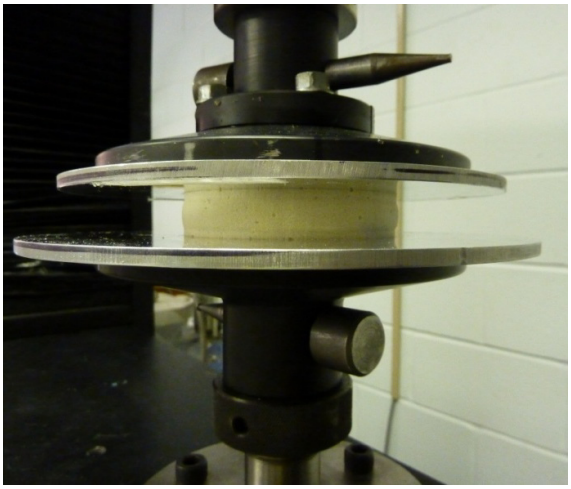


Figure 5-16 : Foam compression test.

The cross head speed was set a 2.5 mm/min, the specimens measured approximately 90 mm in diameter and 20 mm thick. A 50 KN load cell was used to measure compression forces. The compressive strength and the compressive modulus were calculated based on the ASTM D1621 standard. Figure 5-17 shows the results of the compressive strength characterization for different foam densities, isocyanate indices and moulding temperatures. It can be seen that as the index increases the maximum compressive stress in the foam increases. It can also be observed that as the foam density and mould temperature increase, the compressive strength of the final part is improved.

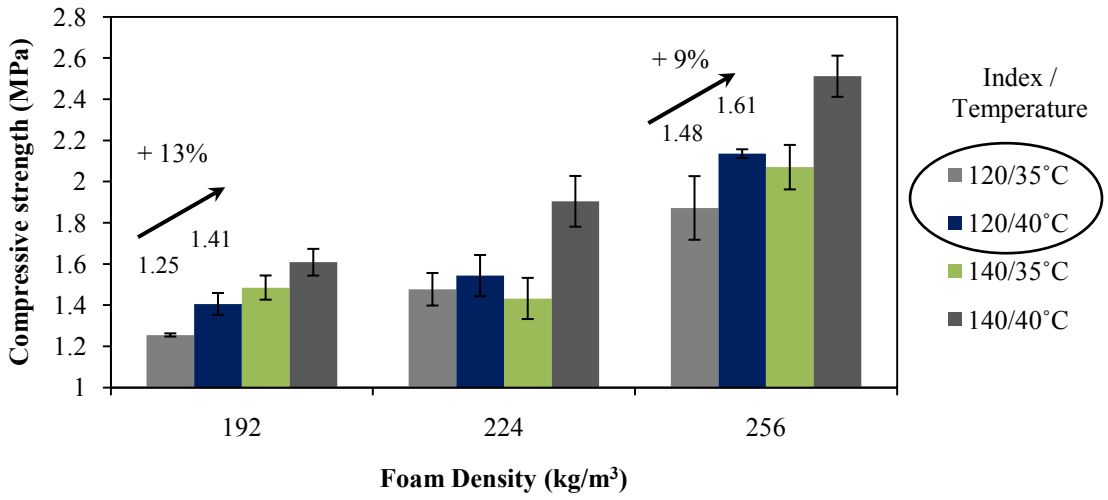


Figure 5-17 : Results of the compressive strength analysis for three dimensional parts at different isocyanate indices and foam densities.

At the higher mould temperature, for the low density and low index case (192 kg/m^3 and 120), the compressive strength value increased 13%. For the higher density and low index case (256 kg/m^3 and 120), it similarly increased 9%. This demonstrates that the mould temperature has a significant effect on the mechanical properties of the foam.

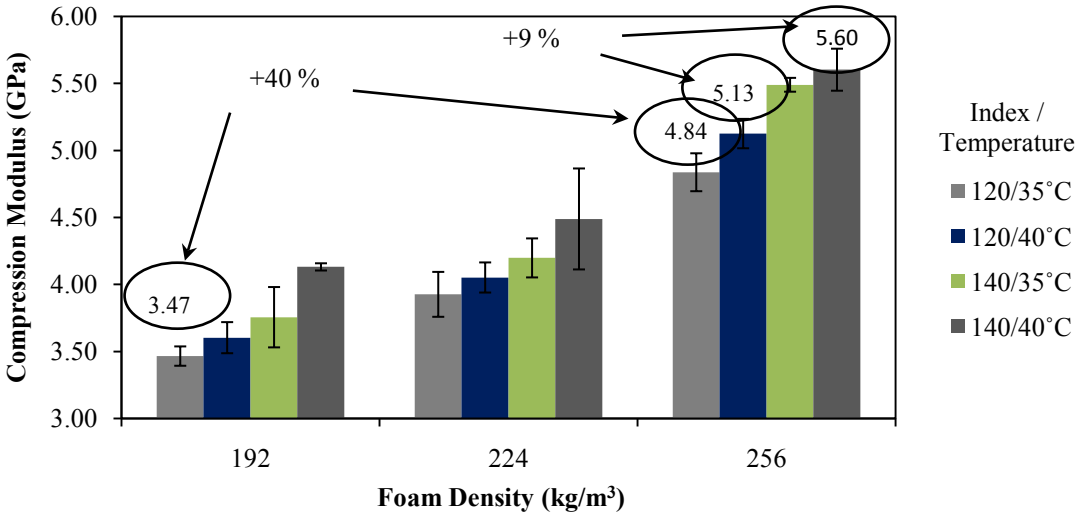


Figure 5-18 : Results of the compression modulus analysis parts at different isocyanate indices and foam densities.

Figure 5-18 shows the results of the compression modulus for this set of experiments. The foam modulus improvements followed similar trends to the compressive strength results, showing a 9.2% increase when the isocyanate index was increased from 120 to 140. The foam modulus also

increased significantly across the range of densities studied. By increasing the foam density 33%, from 192 to 256 kg/m^3, the modulus increased 40%. Again the mould temperature effect seen in Figure 5-17 was again confirmed with the modulus measurements seen in Figure 5-18.

It should also be mentioned that increasing the index reduces the cost of the PUR foam as well, because the isocyanate is approximately 40% lower in cost than the polyol blend.

Another quality indicator for the PUR foam is the glass transition temperature (*Tg*). Using a DMA instrument the *Tg*. was measured for the PUR samples according to the ASTM D7028 standard. The results are reported in Table 5-7. Three samples were measured for each test point.

Table 5-7 : Glass transition temperature (*Tg*) results for three dimensional parts at different isocyanate indices and at high foam density

Target Foam Density (kg/m^3)	**Iso Index (NCO/OH)**	**Mould Temp (˚C)**	**Measured Foam Density (kg/m^3)**	***Tg* (°C)**	***Variation* ± (°C)**
256	120	35	248	102.1	2.5
256	120	40.6	249	104.4	4.9
256	140	35	238	115.4	2.3
256	140	40.6	255	117.7	2.8

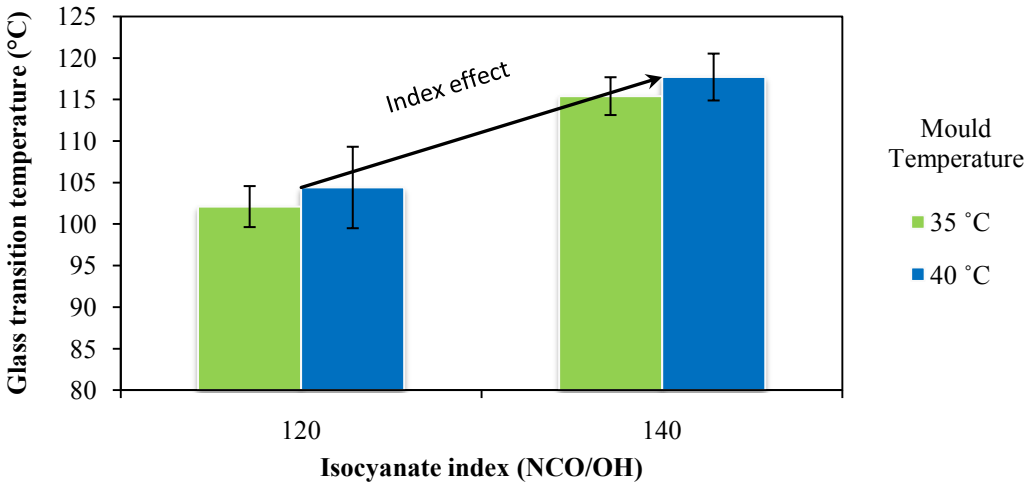


Figure 5-19 : Analysis of the *Tg* for parts moulded at different isocyanate indices and mould temperatures.

There is a significant increase in *Tg* when varying the isocyanate index from 120 to 140, from 102 to 117°C respectively. This represents an increase of 15% in the glass transition temperature. The end use temperature for an exterior application of a black component exposed to natural solar conditions was measured at 70°C. during a durability test completed in Arizona by Decoma International [44]. Based on these results a practical specification was established with a target end use temperature limit of 90°C. This skin is a co-extrusion made with a base layer of blended polycarbonate and ABS with a thin cap layer in Acrylic. From literature, the deflection temperature for this thermoplastic tested at 0.46 and 1.8 MPa according to the ISO standard 74 A and 7 B was reported at 126 and 105°C respectively. Therefore, this blended thermoplastic should resist negative temperature effects at the target temperature. Because the *Tg* for the PUR foam and the heat deflection temperature for the thermoplastic are relatively close, there should be good compatibility with respect to thermal exposure in the range suggested to 90°C. If the desired exposure temperature would increase beyond 90°C it may be necessary to increase the *Tg* of the constituent components.

5.5 Study of sandwich foam composites moulded in a panel mould

The analysis carried out during this final stage of the research focused on the fibreglass reinforced sandwich structure. This study aims the optimization of the resin formulation to improve fibre wetting and therefore the final mechanical properties of the foam. By narrowing down the variables used in the previous experiments, a new plan of experiments was conceived to

evaluate the impact of resin formulation on mechanical properties of the sandwich composite. This experiment focused on varying only two variables: the isocyanate index and the foam density. A total of six injections were completed. From these six parts, three samples were prepared for each of the following mechanical tests shown in Table 5-8.

Table 5-8 : Material tests performed on moulded sandwich composite samples.

Property	Direction	Description	Standard
4 Point Flexural Test	0°	Used to determine the flexural strength, modulus, facing shear stress and failure mode.	ASTM C393 ASTM D6272
Tensile Test	0° and 90°	Used to determine the tensile strength and modulus of the composite and facings.	ASTM D638

According to the previous results, the mould temperature was set at 37.8°C for both the upper and lower moulds. Although the mechanical propertied for the foam increase with increasing mould temperature, the flowing behavior is negatively impacted as seen in the density variation study, as well the blowing nature of the foam speeds up resulting in an increase in visible air bubbles left in the part. The reinforcing fabric used had an areal weight of 678 g/m^2. The specifications of the glass fabric are listed in Appendix B. The warp direction followed the length of the panel and the weft surface was placed directly on the thermoplastic skin. The UV adhesive used was the CB601 developed by Inortech Chimie (see Appendix B).

Approximately 30 g/cavity/side of the adhesive was sprayed on the thermoplastic skins for total of 60 g per part. The UV adhesive was cured in the UV chamber described in section 3.2.2 at a distance 30cm and a speed of 45 mm/s. The moulding parameters used in this plan of experiments are listed in Table 5-9. In this case the foam density was varied from 192 to 256 kg/m^3, while the isocyanate index was chosen at 120 and 140.

Table 5-9 : Experimental design for the panel mould using glass fibres.

Part cavity	Trial	Foam Density (kg/m^3)	Iso Index (NCO/OH)	Ratio (ISO/Poly)	Mass (kg)
1	1	256	120	0.898	6.29
2	2	244	140	1.048	5.69
3	3	192	140	1.048	4.88
1	4	256	140	1.048	6.29
2	5	244	120	0.898	5.69
3	6	192	120	0.898	4.88

Mechanical properties of the six moulded components were then characterized and linked to the foam density and isocyanate index.

5.5.1 Four point flexural tests

The first characterization carried out on the moulded sandwich parts was the four point flexural tests. These tests were based on the ASTM C393 and ASTM D6272 standards which propose the following equations to calculate the elastic modulus (E_f) of the sample.

$$E_f = \frac{0.21xL^3xm}{bxd^3} \tag{5-2}$$

Where:

L = length of the support

m = slope of the tangent to the bending curve

b = width of the sample

d = height of the sample (i.e. thickness)

The measurements were carried out on a mechanical testing equipment (MTS) using a custom four point flexion fixture. The span was set to 450 mm for the lower supports and 150 mm for the upper ones. The experimental setup used for this characterization is shown in Figure 5-20. The photograph in Figure 5-21 shows a loaded sandwich foam specimen just before failure. There were two types of failure modes observed in the eighteen tests. The first mode is buckling of the thermoplastic skin at the middle of the sample, as shown in Figure 5-22. The second failure mode was a shear break of the foam followed by delamination of the fibres and thermoplastic skin as shown in Figure 5-23. The location of the second failure mode was always under the left upper blade. It was observed that the pivot action of the upper left support (see Figure 5-22) created a local stress concentration in the samples. As a result, the majority of the tested samples failed at the same location as shown in Figure 5-23.

Figure 5-20 : Experimental setup used for the 4 point flexure tests.

Figure 5-21 : Flexure test just before failure of the sample.

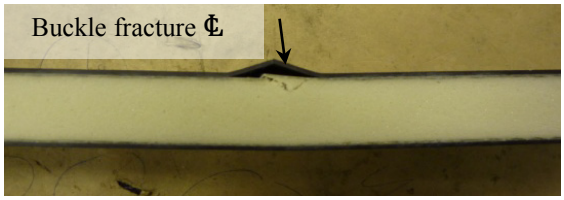


Figure 5-22 : Skin failure by buckling of the thermoplastic skin.

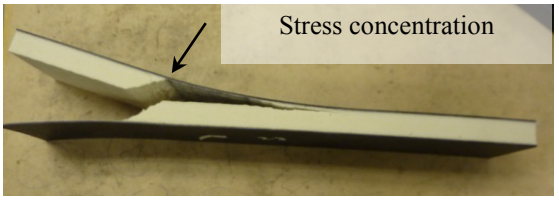


Figure 5-23 : Sample failure due to shear stress of the composite skins.

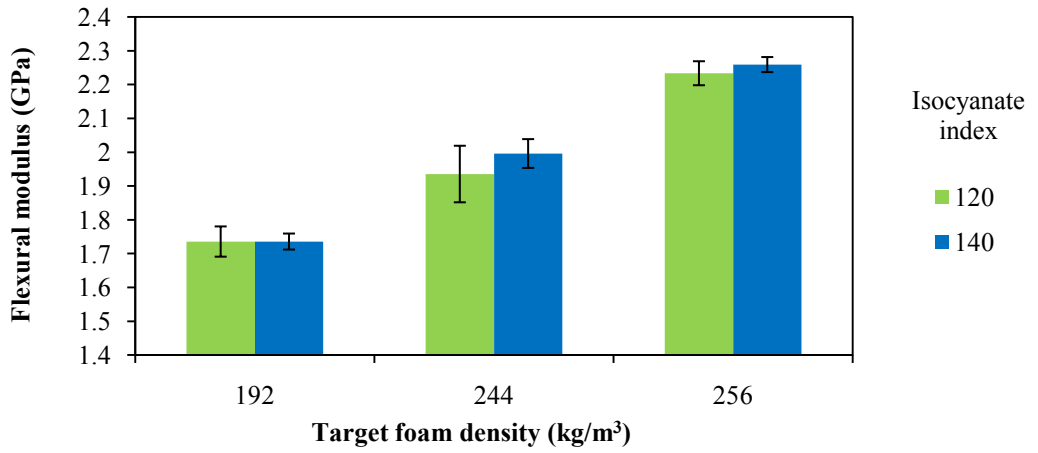


Figure 5-24 : Flexural modulus of the sandwich foam for different isocyanate index and foam densities.

Figure 5-24 summarizes the results of the eighteen mechanical tests carried out on glass reinforced foam samples. The graph illustrates that the flexural modulus increases significantly as the foam density increases. This suggests that the bonding between the fibres and the matrix improves when density of the foam is increased. When looking at the density ranges from 192 to 256 kg/m^3, there was a 29% improvement in flexural modulus. On the other hand, the isocyanate index has a smaller impact on flexural modulus of the sandwich composite. This confirms the observations of the previous plans of experiments.

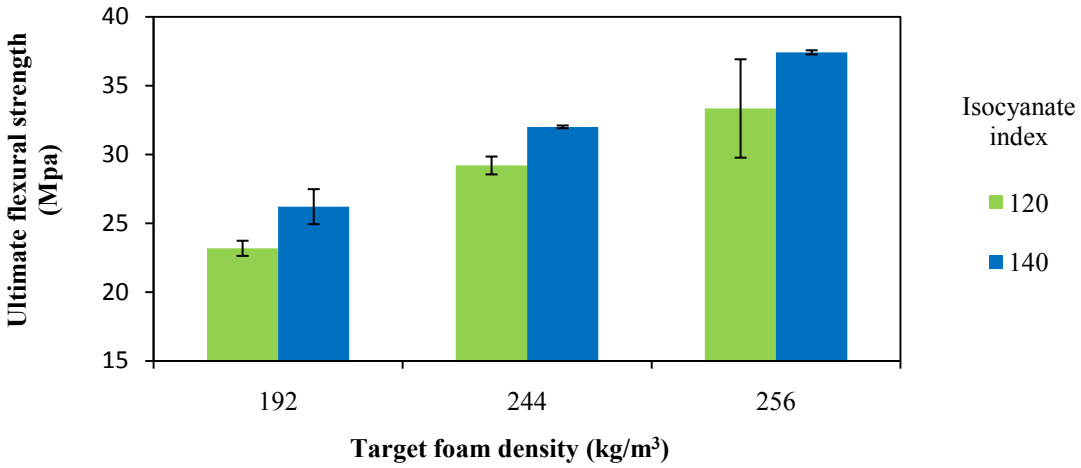


Figure 5-25 : Ultimate flexural stress at break for the sandwich varying Index and density.

Figure 5-25 shows the results of the flexural strength of the foam composite panels reinforced with glass fibres. Again, two effects are observed on the flexural strength while increasing the foam density or isocyanate index.

An increase of 43% was obtained when the foam density was varied from 192 to 256 kg/m^3. This is consistent with the results achieved by Sharaf et al. [15]. For isocyanate index, only a 10% increment was obtained when varying the index from 120 to 140.

5.5.2 Tensile Testing

Tensile properties are also important for composite panels, mainly in the attachment points. The tensile properties of the foam sandwich composite panels were characterized based on the ASTM D638 standard. Due to the thickness of the foam sandwich panels (25 mm), a new set of grips was conceived for holding the samples (see Figure 5-27). The drawings for the grips are in located in Appendix A. A typical tension fracture is presented in Figure 5-27. The breakage of the fibres occurred at the centre of the sample indicating that the grips have no effect on the fracture mode. Tensile modulus and ultimate stress were measured across the two in-plain direction of the composite (i.e. 0° and 90°) as shown in Figure 5-28. From the six moulded panels, a total of thirty six specimens were prepared, i.e. three samples per orientation per panel.

Figure 5-26 : Custom holders for tensile testing the foam sandwich composite.

Figure 5-27 : Fracture of composite below the MTS extensiometer.

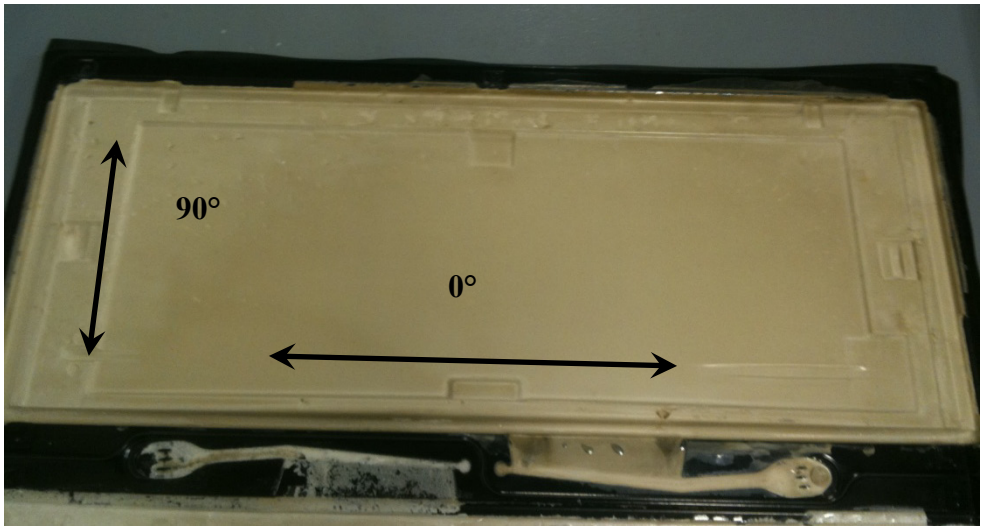


Figure 5-28 : Cutting direction for tensile samples.

The bi-directional stitched glass fabric used in this work has an areal weight of 305 g/m^2 in the 0° and 373 g/m^2 in the 90° direction. To calculate the tensile modulus the stress train curves were plotted for each of the thirty six tests. The curves for two tests are shown in Figure 5-29, for two samples moulded at an isocyanate index of 120 and density of 256 kg/m^3 taken at the 0° and 90° directions. In all of the 36 tests the specimens exhibited a catastrophic tensile failure. The failure mode was brittle and occurred between 1.2 and 3.8% strain.

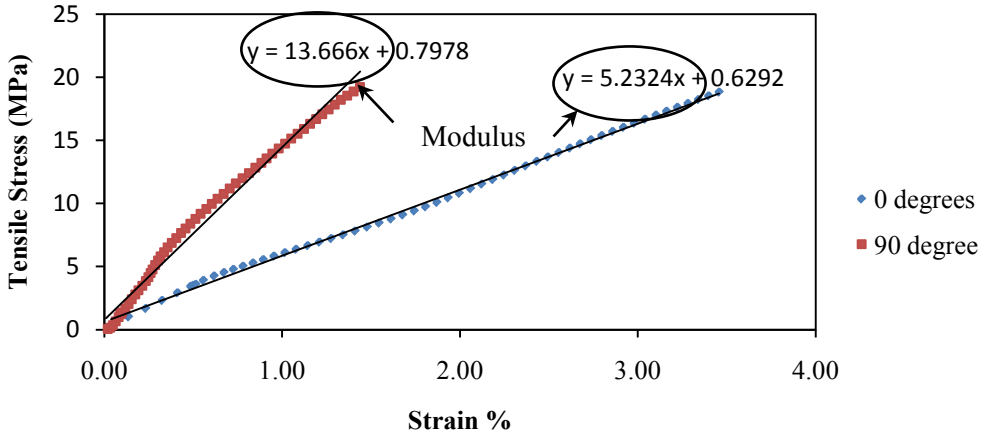


Figure 5-29 : Stress strain curves for tensile tests completed at index 120 and density 256kg/m3 for the two principal fibre directions.

Tensile modulus results for both directions are depicted in Figures 5-29 and 5-30. It can be observed that a small increment in tensile modulus is caused by increasing the foam density. However, no visible impact is observed with the isocyanate index. The increment in modulus is probably linked to a better impregnation of the fibres at the high foam density. Note that the thermoplastic skins play a key role in the traction properties. The tensile modulus of the PC/ABS thermoplastic is around 2.2 GPa [45], which is in order of magnitude of the measured tensile modulus of the sandwich composite. Finally, it can be observed that the higher variability of the tensile modulus is observed at higher density. This observation is in accordance with previous results (see Figure 5-4).

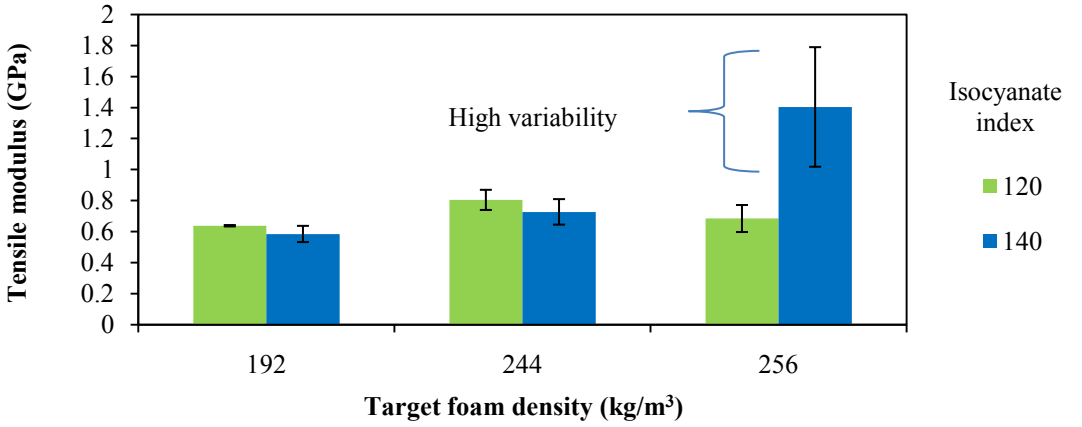


Figure 5-30 : Tensile modulus versus density and Index 0° direction.

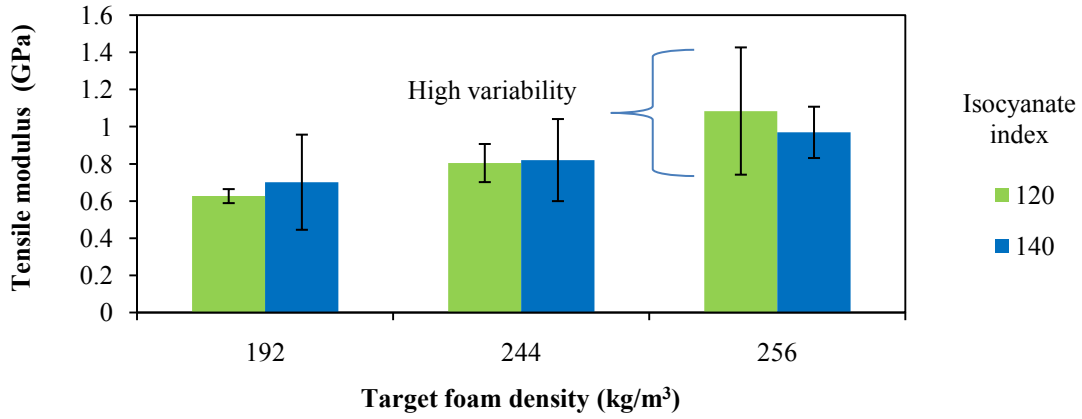


Figure 5-31 : Tensile modulus versus density and index 90° direction.

Figures 5-32 and 5-33 show the ultimate stress measured at 0° and 90° directions respectively. In this case no visible impact was observed with foam density and isocyanate index. The high variability of the results was obtained for these tests. One of the hypotheses for the increased variability is the possibility of a misalignment of the fibres in the sample, since a small misalignment will induce a large effect in the results. Note that, the neck of the specimen is 13 mm wide which corresponds to only five fibre toes. Therefore the number of fibres supporting the load will be inconsistent.

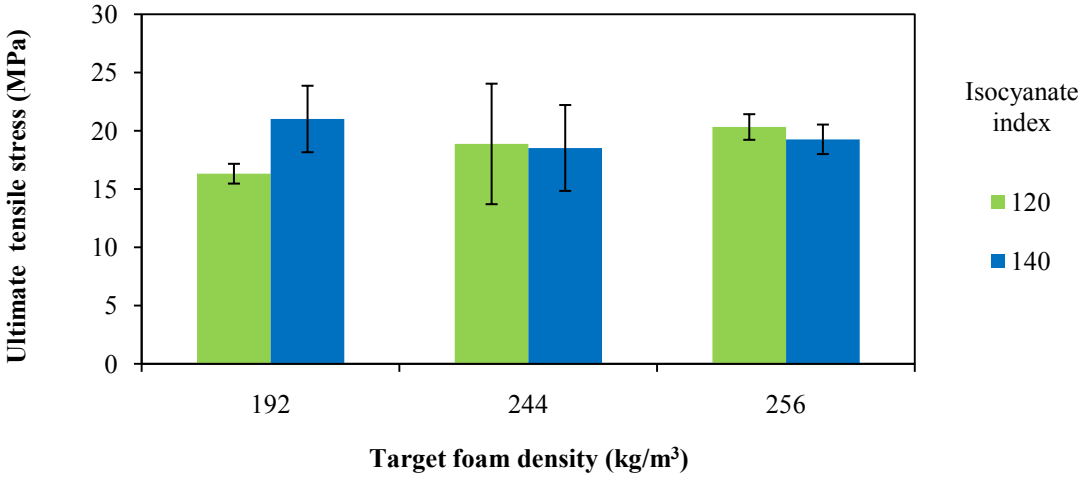


Figure 5-32 : Ultimate tensile stress in the 0° direction.

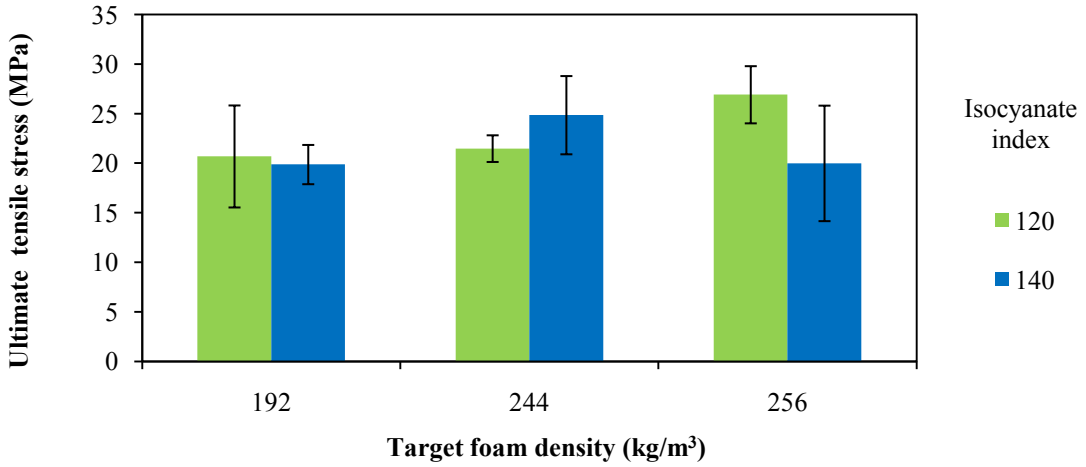


Figure 5-33 : Ultimate tensile stress in the 90° direction.

An improvement would be to increase the specimen neck width to 25 mm therefore the preforming and sample preparation issues will have a reduced effect. This analysis was not conclusive on the impact of the resin formulation on tensile properties of the foam sandwich.

CONCLUSION

The innovative Poly-Foam (PFSC) process studied in this work could present a new processing method to produce high performance sandwich structures that are greener (negligible quantities of VOC's). The process is also capable of producing, with rates up to 45,000 parts per mould set. The process is highly automatable; the use of thermoplastic carrier skins offer both processing advantages (carrier for the fibres) but also simplify the moulding process (reduced cleaning). The final products have a thermoplastic moulded in colour and texture finish requiring no sanding or post painting. Depending on final use of the product properties can be engineered into the thermoplastic skins for weather ability, chemical resistance, temperature resistance as well as colour and texture.

The novelty of the process occurs when the polyurethane foam in injected into the preformed thermoplastic and fibreglass skins creating the final composite sandwich laminate in one step. The nature of the self skinning polyisocyanurate foam makes it possible to create the three dimensional foam cores as well as wet out the dry fibreglass creating the rigid sandwich composite at the same time.

The preforming process developed in this work is also innovative using UV binders to bond fibreglass mats to thermoplastic skins. The UV binders offer a wide possibility of formulating options depending on the thermoplastic substrates selected. This process makes it possible to cure the binders at low temperatures resulting in reduced stresses and reduced skin distortion. This process also lends itself to automation. Robots can be used to apply the liquid binder and automated UV ovens can complete the curing.

The primary objective of this research was to fully characterize this process in order to understand the fibre wetting phenomena and its impact on mechanical performance of the components. A series of equipment was conceived and constructed to measure the foam behaviour under atmospheric and high pressure conditions. The atmospheric free rise apparatus utilized a sonar sensor and thermocouples to monitor the foam development and the exothermic behaviour. With this equipment it was possible to run tests varying the resin formulation and the parameters of the injection system in order to optimize the manufacturing conditions. The learning’s from this investigation were then applied to the next stage of this study, foaming under

pressure. In this case a closed mould was conceived, implementing an impedance sensor, a pressure transducer and thermocouples. As well, this mould had a glass window used to visualize the fibre saturation phenomena in real time. The data collection system developed for this mould records simultaneously, the foam viscosity and gel behaviour using the impedance measurement, as well as the pressure and exothermic behaviour. The results of the second plan of experiments illustrated that the pressure in the foam drives the saturation of the foam, and however there was thickening of the PU skin and laminate in the middle of the experimental design at a density of 225 kg/m3 and isocyanate index of 130. This is encouraging because it is desirable to reduce the density of the core for both economic reasons and where the part weight is critical.

After the free rise and the foaming under pressure experiments were completed, tests were carried out using a 3D panel mould with and without fibreglass. The first tests were used to visually evaluate the morphology of the foam quality and to measure the compressive strength of the foam over a range of densities and isocyanate indices. The parameters established in the earlier experiments were maintained for this set of tests. Also, the glass transition temperature of the foam was investigated over a series of mould temperatures and isocyanate indices. It was discovered that the mould temperature plays an important role in development of the final properties of the foam; however, increasing the mould temperature also reduces the quality of the skin and resulting laminate therefore mould temperature optimization is critical. Finally full composite sandwich structures were moulded using bi-directional mats preformed using the UV procedure. Again the foam density and isocyanate index were varied to evaluate their influence on mechanical properties of the foam sandwich, specifically the flexural rigidity and the tensile strength. Similar to the moulding under pressure experiments, the centre of the experiment yielded a reduction in the variability of the results. Unlike low density sandwich structures where the properties of the core have a small effect on the sandwich properties, in this case the properties of the core had a direct influence on both the rigidity of the composite and the tensile behaviour. This is due to the fact that the properties of the facing are directly linked to the properties of the core.

Throughout the experimentation the analysis has led to an optimum solution for the resin formulation where the skin properties were maximized and the mechanical properties were improved. The optimized formulation was achieved at an isocyanate index of 130 and a density of 244 kg/m^3. This formulation resulted in the improved saturation of the fibres and maximized

skin thickness, the combination of high pressure and increased temperature at gelation resulted in this optimized formation. The moulding temperature of the resin has a direct influence on the glass transition temperature of the PUR foam and requires further investigation.

The characterization techniques developed in this work will make it possible to further optimize the foam formulation for high end applications, opening the doors to aerospace and other high performance uses.

PERSPECTIVES AND FUTURE WORK

The first phase of this work will open the door to many structural and semi structural applications; such as, load floors, balconies, roof systems etc. Moving forward, there are many areas where this process and resulting products could be optimized: through the use of greener bio-resins and bio-fibres. For aerospace acceptance the next step will be to determine the flammability behaviour and possible introduce new materials to enhance this property. As well, the surface skin material will require optimization or direct change to the polyimide family. This would result in further development of the UV binder. With the existing process, foam core and PUR skin optimization should lead to reductions in weight and improvements in mechanical properties.

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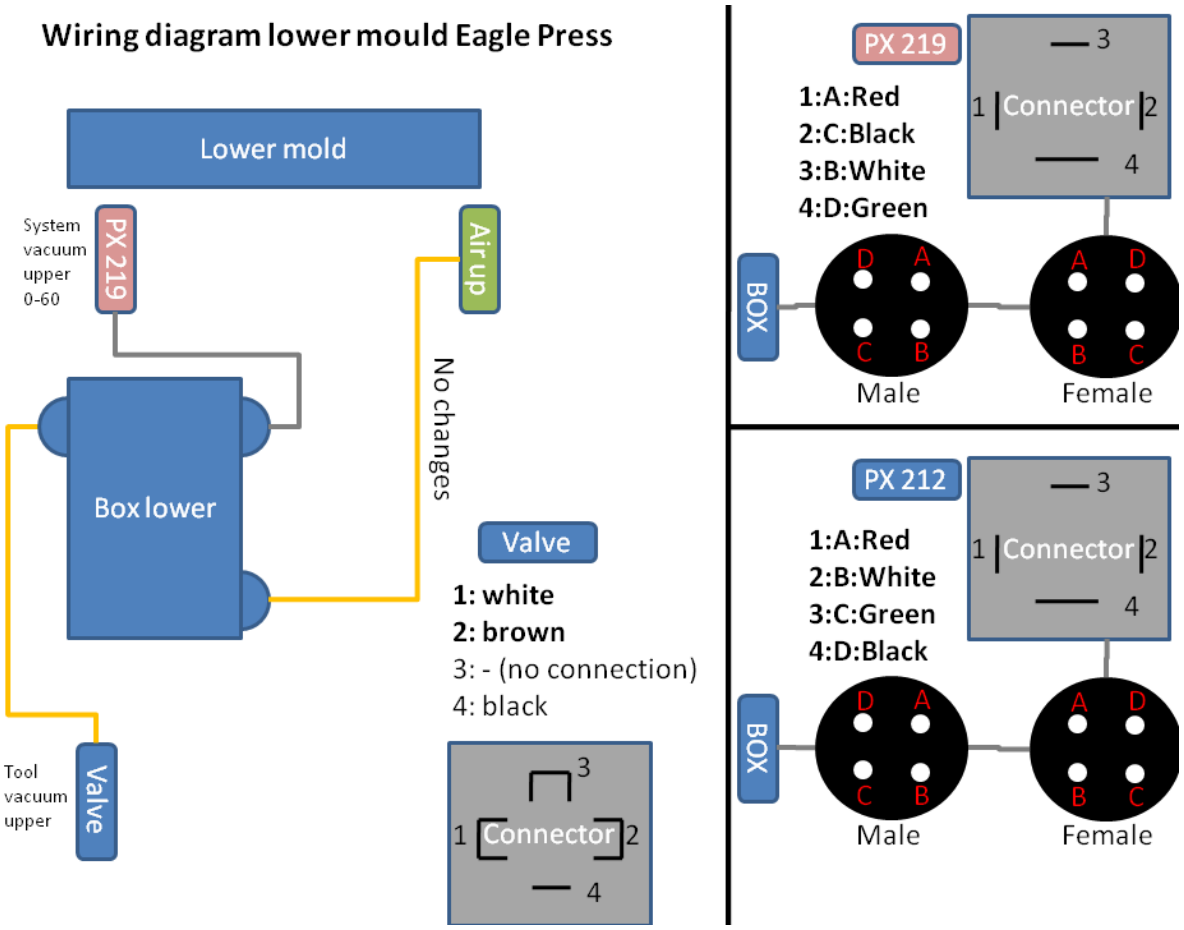
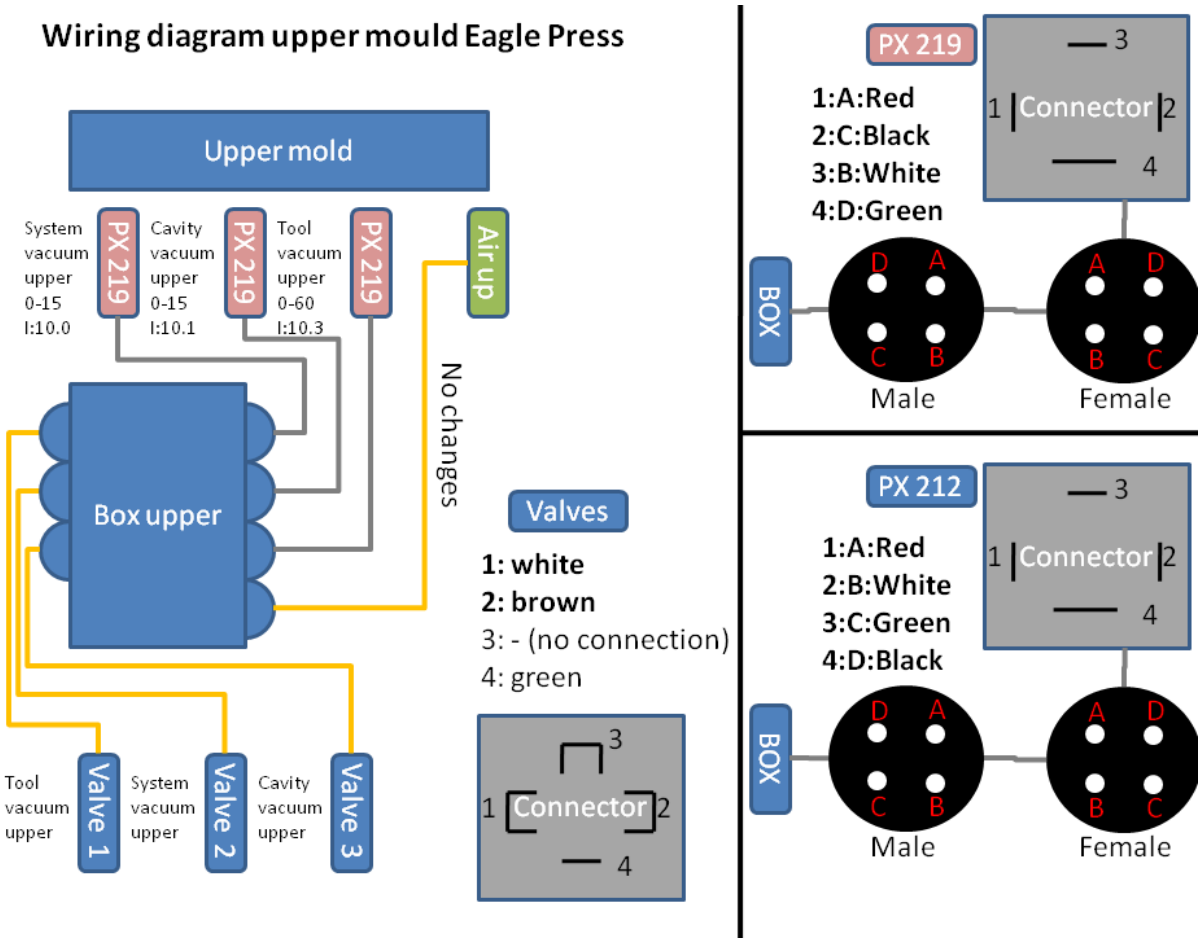
APPENDICES

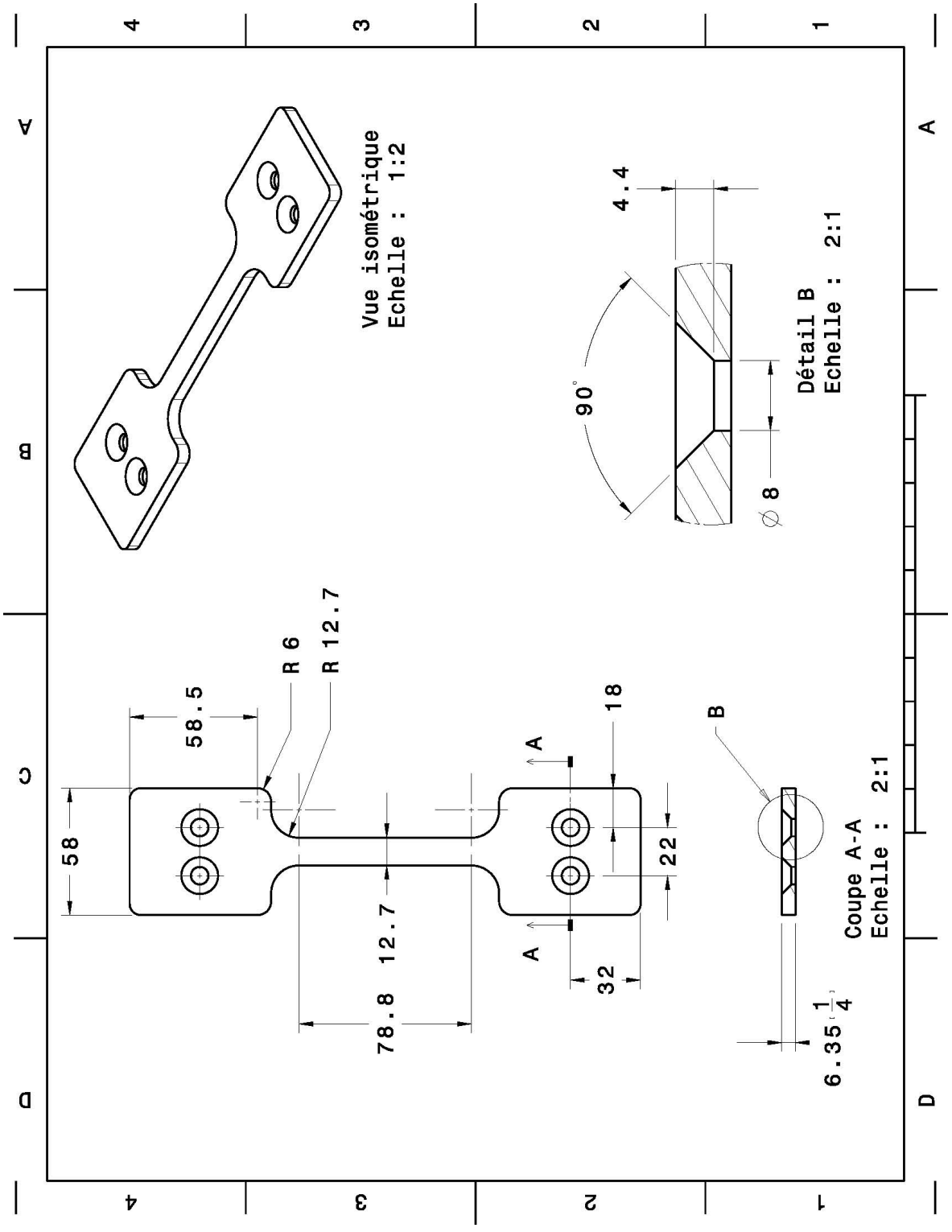
APPENDIX A: Drawings



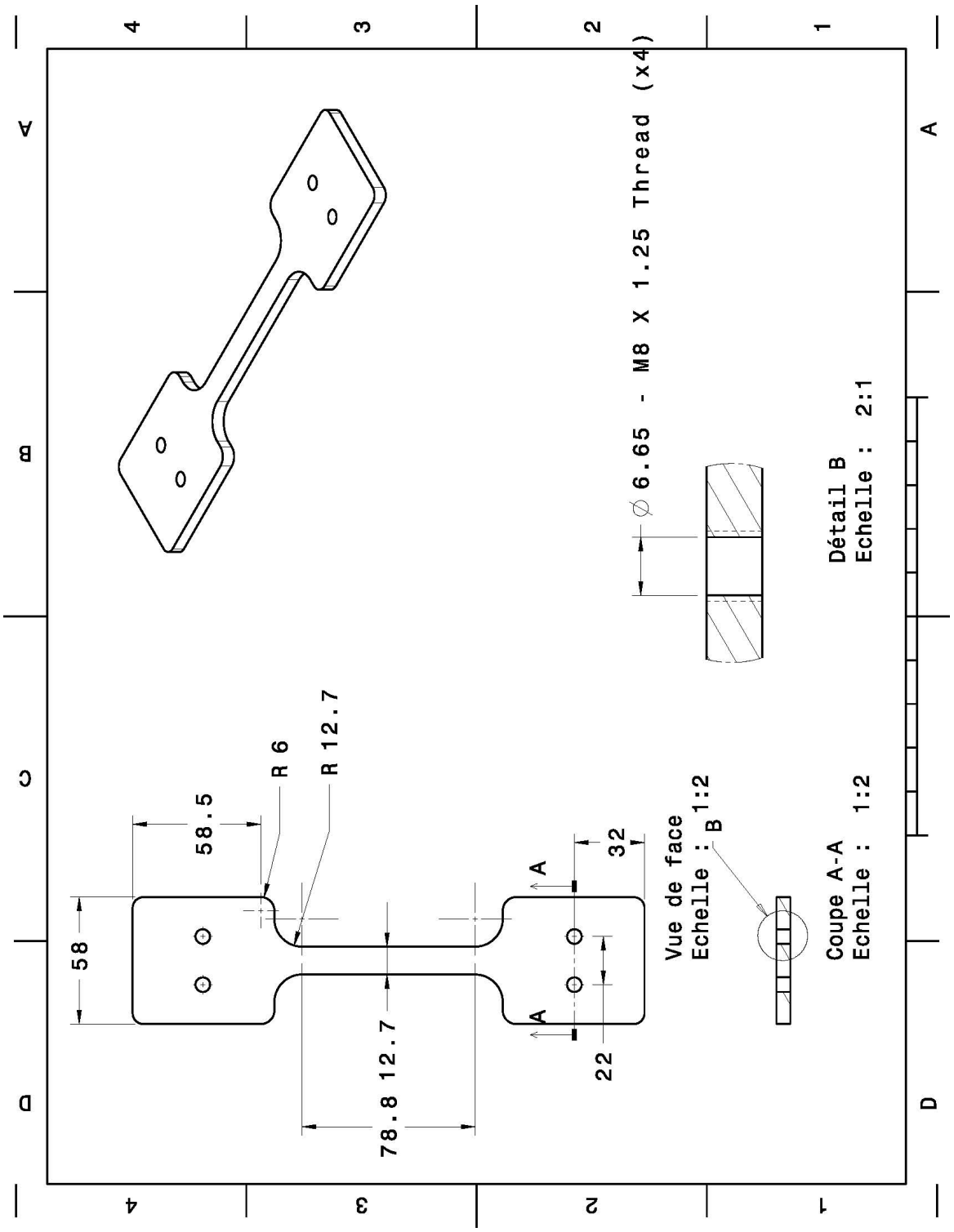
a) Changes to the wiring for the Eagle Press to accommodate the new mould mounted pressure transducers on the lower bolster.



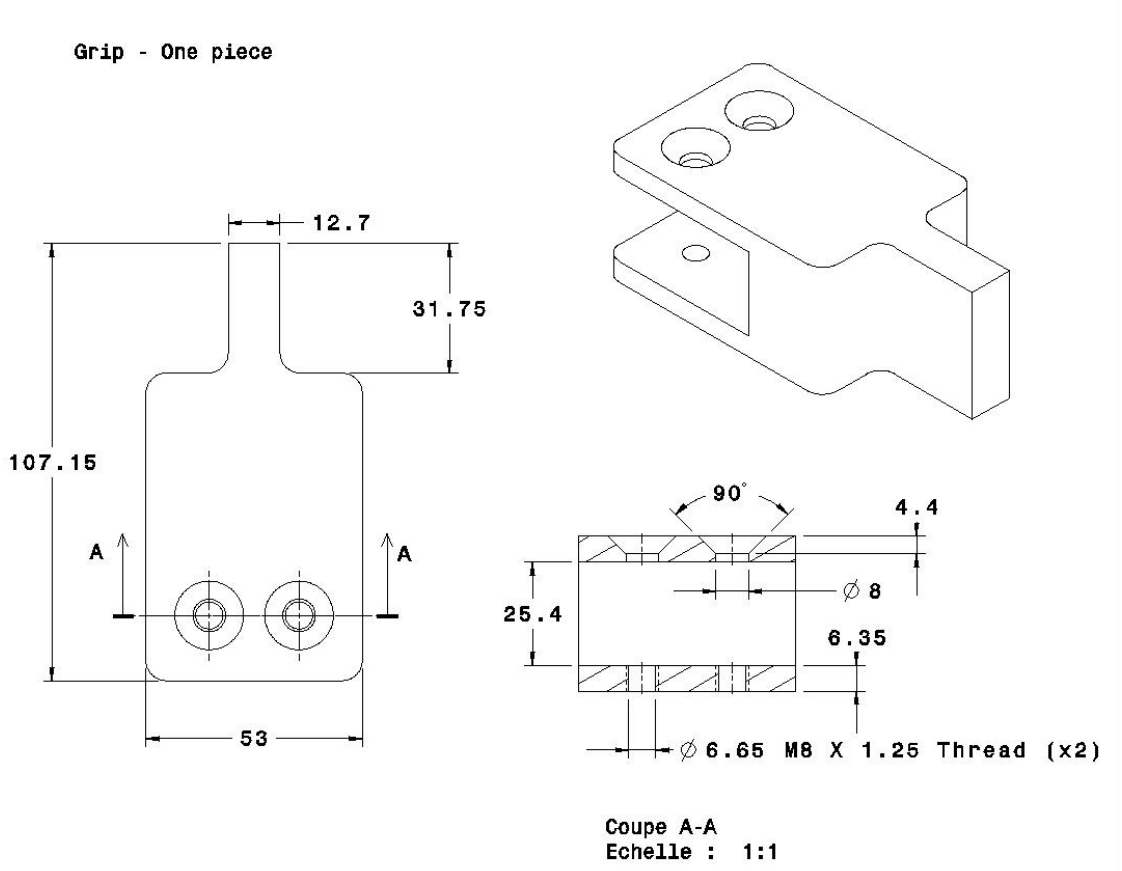
b) Changes to the wiring for the Eagle Press to accommodate the new mould mounted pressure transducers on the upper platen.



c) Upper cutting guide used to manufacture Tensile Bars from the composite sandwich structure panels.



d) Lower cutting guide used to manufacture Tensile Bars from the composite sandwich structure panels.

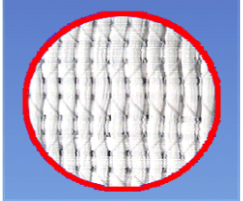


e) One piece grip used to hold the Tensile Bars in the MTS machine. Two identical grips are needed, manufactured in 7076 Aluminum

APPENDIX B : Materials

Consistently fgi The Best

Knitmat® 0°/90°



0° - 90° Chop

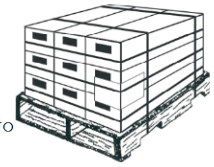
Knitmat® 0°/90°

Knitmat® is a High Strength Stitch bonded product. Stitch bonding mechanically combines warp (0°) and weft (90°) roving. **Knitmat®** products are available with and without chopped glass strand. Combinations with glass, polyester, and other veils, along with CSM are available upon request. The resulting no crimp product is extremely conformable, offering fast wet out, and excellent process-ability due to high dry wet strength. **Knitmat®** is ideal for hand lay up molding, resin infusion process, SRIM, RRIM, and SCRIMP® processes. FGI's proprietary sizing allows the end user complete compatibility, with Polyester, Vinyl Ester, Epoxy, and Polyurethane resin systems.

Product Data

S2000 Nominal Weight oz./sq. yd.	20.44
0°/90° Weight oz./sq. yd.	9.10, 11.01
Nominal Thickness	0.050
Roll Length Yards	85
Roll Length Meters	
Weight per inch of Width	3.6 lbs.

* Optional styles available upon request — Special pricing may be applicable.



Packaging Data

All rolls individually boxed and palletized according to size and weight.

Typical Test Data

Properties	0° (ksi)	90° (ksi)	Modulus (msi)
Tensile	34.80 - 41.70	21.30 - 48.10	2.30 - 2.60
Compressive	38.70 - 50.10	23.90 - 50.20	2.20 - 3.10
Flexural	55.60 - 66.00	34.70 - 74.90	1.80 - 2.10
Glass Content by Weight	47 - 55%	47 - 55%	47 - 55%

The information herein is to assist customers in determining whether our products are suitable for their applications. Nothing herein shall constitute a warranty, expressed or implied. Relative values shown are accurate to the best of our knowledge

Rev. 03 04/08/04

Fiber Glass Industries, Inc.
69 Edson Street Amsterdam, NY 12010 Tel. (518) 842-4000 • Fax (518) 842-4408
www.fiberglassindustries.com

a) Technical data sheet for the bi-directional stitched mat used in this work.

Permabond LITE-LOK® 491

Light Curable Adhesive

TYPICAL APPLICATIONS

- Bonding fiberglass laminations
- Bonding plastic assemblies

FEATURES & BENEFITS

- Fast cure under low energy visible light
- Cures through UV absorbing surfaces
- 100 % solids, no solvents or by-products
- Good thermal cycling resistance
- Versatile adhesion

GENERAL DESCRIPTION

LITE-LOK 491 is a visible light curable adhesive designed primarily to bond plastics and fiberglass laminations. The cured adhesive has good impact resistance, and good temperature and humidity resistance. The material has very good adhesion to many plastic substrates such as acrylic, ABS, PVC, SAN, and polycarbonate. It has good resistance to thermal cycling without loss of adhesion.

PERMABOND, a division of National Starch & Chemical
10 Finderne Avenue, Bridgewater, New Jersey 08807
Applications Development & Customer Service: 1-800-370-9647
Fax No.: 1-908-575-7203
www.permabond.com

PHYSICAL PROPERTIES OF THE UNCURED ADHESIVE

Properties	
Generic Base	Acrylate Mixture
Color	Yellow Liquid
Solids, %	100
Viscosity at 25°C, cP	approx. 20,000
Specific Gravity	1.07
Flash Point,°C (°F)	> 100 (>212)
Shelf Life stored at or below 27°C (80°F), months	6

RECOMMENDED CURING CONDITIONS

Optimum cure is obtained when LITE-LOK 491 is exposed to high intensity visible light or long wavelength UV light. The peak reactivity of the product is from exposure to light from 385 nm through 420 nm. The time needed for curing is a combination of many factors. Some of these are:

- The thicker the substrate, the longer the exposure time needed for curing.
- The more UV light absorbing that the substrate is, the longer the exposure time needed for curing.
- The lower that the intensity of the UV light source is, the longer the exposure time needed for curing.
- The farther the distance of the product from the UV light source the longer the exposure time needed for curing.

Typically, LITE-LOK 491 will cure after a UV light exposure from two to five seconds, when cured at or near the focal point of a high intensity light source.

To achieve complete cure, all of the adhesive must be exposed to the UV light source.
LITE-LOK 491 is designed for use <0.040 inch coating. LITE-LOK 491
cures best when cured between two substrates as an adhesive. Excess exposed product may exhibit a slight surface tack.

SURFACE PREPARATION

LITE-LOK 491 bonds well to many untreated surfaces. However, adhesion is often improved by surface prepartion before bonding. The surface should be free of contamination such as dirt, dust, grease or oil. An alcohol wipe is suitable for cleaning most surfaces. Optimum strength is obtained by abrading the surface followed by a solvent wipe to remove any loose particles. Polyolefins must be corona treated, or flame treated before bonding.

APPLICATION & DISPENSING

LITE-LOK 491 is best applied by extruding the product onto the substrate to be sealed or bonded.
Sufficient product must be applied to seal all gaps, and completely coat the part to be bonded or sealed. After dispensing onto the part, the product should be cured as soon as possible to prevent any pre-reaction with ambient light.

LITE-LOK 491 may be applied via a pressure pot, or piston pump dispensing system. All fittings and tubing used in the dispensing system must be opaque to light. If the product is transferred from a large container to a smaller hand held dispensing bottle, that bottle must be light impenetrable. (see Storage & Handling).

STORAGE & HANDLING

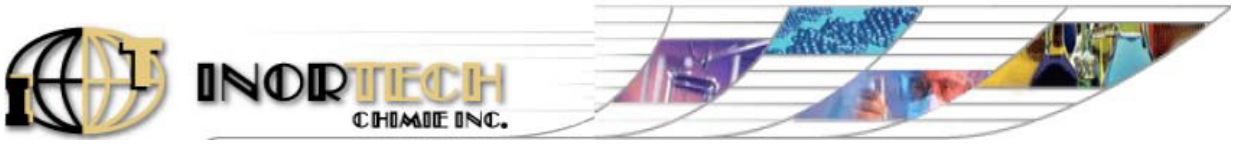
Protect the adhesive from exposure to light, especially UV light. Keep container closed while not in use. This is best done by opening the container for only the minimum time necessary, and opening only under yellow or red light. Any containers used for dispensing the adhesive must be light impenetrable. Store container in the dark at temperatures at or below 27°C (80°F). Do not freeze.

Skin contact should be avoided. Handling should be done using Neoprene(R) or nitrile rubber gloves. Unreacted material can be cleaned up using acetone. If skin contact occurs, the affected area should be washed thoroughly with soap and water. Eye protection against UV light should be worn whenever the product is being used. Eye contact should be treated by thoroughly washing with water followed by medical attention. Aprons should also be used. Adequate ventilation is necessary to prevent inhalation of vapors.

Curing equipment must provide the proper protection against UV light.

FOR INDUSTRIAL USE ONLY. KEEP OUT OF REACH OF CHILDREN.

b) Technical data sheet for the UV adhesive manufactured by Permabond, used in this work.



INORMER ADHESIVE CB 601

GENERAL

Inormer Adhesive CB 601 a solvent free 100% solid urethane acrylate based UV curable adhesive. Lasting bonds form in seconds to both flexible and rigid substrates such as PVC, polycarbonates, polyurethanes, PET & PETG. Bond strength on PVC and polycarbonates usually exceed the strength of those substrates.

PHYSICAL PROPERTIES

Technology	Urethane
Chemical type	Urethane acrylate
Appearance (uncured)	Transparent
Components	One component requires no mixing
Viscosity	14022 cps at 25C 10212 cps at 30C 2285 cps at 60C
Cure	Ultra violet/Visible light
Reactivity	UVV = 172 mJ/cm2
Specific Gravity	1.05

APPLICATIONS

Inormer Adesive CB 601 is designed for bonding carbon and glass fiber to polycarbonates where large gap filling capabilities are desired. The thixotropic nature of

Inormer Adesive CB 601 reduces the migration of liquid product after application to the substrate.

INORTECH CHIMIE INC., 3014 Anderson St., Terrebonne, QC, J6Y 1W1 Toll: (800) 661-2064 Phone: (450) 621-1999, Fax: (450) 621-1996

STORAGE CONDITIONS

Store material in a cool dark place when not in use. Repeated or continuous contact with adhesive may cause irritation and should be avoided. Replace lid immediately after use Product has a one year shelf life when stored below 30 C in the original unopened container.

PACKAGING

In 200 kg Drums or as per customer's requirement.

SAFETY & HANDLING

Inormer Adhesive CB 601 should be handled in accordance with good industrial practice. Detailed information is provided in the Material Safety Data Sheet (MSDS).

REGISTRATION

Inormer Adhesive CB-601 is listed on the following inventories: **Australia: AICS Canada: DSL Europe: polymer, monomers on EINECS Japan: MITI Korea: ECL USA: TSCA**

The information presented herein is believed to be accurate and reliable, but is presented without guaranty or responsibility on the part of Inortech Chimie Inc. It is the responsibility of the end user to verify and validate this information and the suitability of this product in their own systems. Inortech Chimie inc. declines all responsibility for the use of this product in any systems.

Les informations ciincluse sont, nous le croyons, précises et conforme; mais elles sont présemtées sous toute réserve et sans garanties. Il est donc de la responsabilité de l'utilisateur de bien vérifier ces données et de validé ces informations et de la pertinances de ce produit dans l'utilisation désirée. Inortech Chimie inc. ne sera aucunement tenu responsable de l'utilisatiion de ce produit dans tous systems.

INORTECH CHIMIE INC., 3014 Anderson St., Terrebonne, QC, J6Y 1W1 Toll: (800) 661-2064 Phone: (450) 621-1999, Fax: (450) 621-1996

c) Technical data sheet for the UV adhesive manufactured by Inortech Chimie, used in this work.